STUDIES ON INORGANIC ION EXCHANGERS AND LIGAND ION EXCHANGERS

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CERTIFICATE

This is to certify that the work embodied in this thesis is original and suitable for submission for the award of Ph.D. degree in Chemistry.

J P Rawat

(J.P. Rawat)

DEDICATED to my brother
Dr. S. Q. M. RAHMOONPURI
AND
My Parents Without Whose Sacrifice I Could
not have undertaken this Work

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INTRODUCTION

Analytical chemistry is permeating in all fields of human endeavour. From biology to medicine, geology to occeanography, nuclear to space research etc. its application are manifold. Though an infant branch of chemistry it has established itself as perhaps one of the most important, useful and applied branches of science.

There are three basic facets of Chemical Analysis:

a) Identification: This involves the characterization of the basic identity of a compound without which further analysis would be meaningless. This art is all the more innovative, as in the analysis of complex mixtures.

b) Determination: The quantitative aspect is termed as determination. Here, the amount of a constituent present in the sample is determined.

c) Separation: Separations find important applications in medicine, agriculture, environmental analysis etc. Separation is basically a pretreatment method which usually precedes any qualitative or quantitative analysis. Pretreatment of most samples obviates the interferences of other substances. Separation involves both classical and modern techniques. Precipitation and distillation are both examples of the classical methods. The modern techniques may be classed as below:

a) Solvent Extraction

b) Paper and Thin Layer Chromatography

c) Gas chromatography

d) Liquid chromatography

e) High performance (or high pressure/speed) liquid chromatography

f) Ion-Exchange chromatography

g) Ion chromatography

h) Electrophoresis

Of all the above, ion-exchange has carved a niche of its own, and has come out to be a very valuable technique especially where the separation of ionic species is required. It is also one of the most versatile methods of separation.

In 1850, Thompson and way, two English chemists, discovered 'base exchange' (cation exchange) in soil. The first synthetic industrial ion exchanger was prepared in 1903 by Harm and Rumpler, two German Chemists. A spectacular revolution began in 1935, with the discovery by two English chemists, Adams and Holmes, that crushed phonograph records exhibit ion-exchange properties. The study of this remarkable effect led the inventros to the synthesis of organic ion-exchange resins which had excellent properties over the earlier ones.

Ion-exchange can be applied to micro as well as macro analysis. This technique has been used to solve earlier apparently unsolvable problems such as separations of rare earths[1-

for the isolation and identification of the new transuranium element[8-13], for the enrichment of isotopes[14-20] etc. It has also been widely used for organic substances such as Amino Acids[20-28], peptides[29-30] proteins[31], nucleic acids[32], alcohols[33-34], glycols[35,36], carbonyl compounds[23,33,37,38] carbohydrates and derivatives[39-43], ethers[38-44], amines[44-46], hydrocarbons[38-47] and phenols[38-48] have been separated on ion-exchange columns.

The field of environmental pollution has assumed perhaps the greatest importance in our daily lives. Though air pollution, water pollution and soil pollution are all equally important, water pollution has always commanded greater interest. Pollution has no natural causes and has been totally created by the civilizations over the ages in their quest for a better life. Ion exchange has emerged as one of the frontier areas in the field of analysis pertaining to water pollution. Water is the 'Universal solvent' and has the most excellent solvating properties than all other solvents put together. In its natural state it always contains dissolved impurities. A thorough chemical analysis of water reveals that most of the elements can be found in samples taken from lakes, rivers and sea. It also contains a wide multitude of organic compounds which are either miscible with water or have high aqueous solubility. Ion exchange can be applied to water analysis as it is basically a separation and concentration technique.

It is being significantly utilized in water analysis to concentrate the trace quantities and separate[49,50] one substance from the other.

The industrial applications of ion exchange continue to increase at an exponential rate. Newer and newer uses are actively being sought day after day. Ion exchange finds paramount importance in photography where it can be used to recover silver from photographic waste waters and also from silver chloride[51], which is unwisely released in drains as waste. This is popularly accomplished as the precipitation of silver as $Ag_2(S_2O_3)_3^{4-}$ on an anion exchange column. This process suffers from difficulties of incomplete regeneration and low K_d values for silver in the presence of large concentrations of thiosulfate.

Siegel and Degens[52] applied principles of ligand exchange chromatography to adsorb and concentrate amino acids from sea water. Phenols, aromtic hydrocarbons, triphenylaniline and many other organic compounds have been determined in industrial waste waters by HPLC using ion exchange pellicular packings[53].

Soil, the most widely, inexpensive and easily available material was for the first time recognised as an ion exchange material by two agricultural chemists Thompson[54] and Way[55]. As mentioned earlier they discovered this phenomenon by the name of 'base exchange', in soils. The exchange involved equivalent quantities of replaceable and replaced ions. It was established

as early as 1854, that aluminosilicates were responsible for this exchange[56,57]. According to Lamberg[58] and Wergner[59] the material responsible for this exchange were mainly clays, zeolites, gluconites and humic acids. The inception of organic resins pioneered by Adams and Holmes remove many of the difficulties encountered with zeolites and clays[60]. The resins which exhibit highly improved properties over the previous largely natural products are stable towards acids and elegant to handle. Their structure can be varied as desired. They are finding increasing use in industries and laboratories for the separation and subsequent recovery of metal ions, de-ionization of water, preconcentration and concentration of electrolytes and in the elucidation of the reaction mechanism of a wide variety of chemical reactions[61]. This last aspect is both of paramount fundamental and applied interest. The applications of these ion-exchangers were so rapid and so very diverse that the development of the theoretical principles was retarded for a long time and was almost overshadowed by the experimental progress.

However the ion exchange resins, though unique were certainly not versatile. They also suffer from disadvantages under certain experimental conditions. These resins decompose at elevated temperatures and under the influence of ionizing radiation. This led to a rethinking amongst chemists and a renaissance of an interest towards inorganic based exchangers.

Apart from their far improved temperature resistance and complete immunity to ionizing radiation the inorganic ion exchangers possess a rigid molecular framework. This stiffness of structure leads to enhanced sensitivity and selectivity for the separation of ions on the basis of their pore size. They can also be used as ionic or molecular sieves. Being resistant to high temperature they can be satisfactorily used in reactor technology. Inorganic ion exchangers also find use in the analysis of alloys[62,63], and silicate rocks[63,64], separation of metal ions from drugs[65-67] and notably in the detection of iron and molybdenum[68,69].

The studies on synthetic inorganic ion exchangers commenced in 1943 with the discovery of the insoluble compound, Zirconium Phosphate and its application to the separation of Uranium and Plutonium from fission products[70]. The earlier work through 1962 has been excellently summarized in a brief monograph by Amphlett[71] entitled 'Inorganic Ion-Exchangers', which has become a classic and has stimulated impetus for subsequent research in the field. A set of reviews by Pekarek and Vesely[72,73] summarizes relevant work done in the period between 1963 and 1970. The theoretical aspects of inorganic ion exchangers have been comprehensively summarized by Marinsky[74], who himself has done some pioneering work in the field. The synthesis and applications of inorganic ion exchangers has been reviewed by Walton[75-79]. Reviews on the applications of inorganic ion exchangers have been edited by Marinsky[80] and Walton[81]

Clearfield, one of the towering giants of the field has covered further work on synthetic inorganic ion exchangers in a very recent monograph[82].

The ion exchange properties of some of the more important ion exchangers of the Zirconium phosphate class have been summarized in table 1.

Table 1

Synthesis and Ion Exchange Properties of Multivalent Metal Salts

S.No.	Material	Type of Exchanger	Composition	Experical formula	I.E.C.	Selectivity	Refs.
I.	Zirconium Salt						
1.	Zirconium Phosphate	Amorphous	P:Zr=0.5:2.1	$Zr(OH)(PO_4)$ $ZrO(HPO_4)$ $Zr_3(PO_4)_4$ $Zr(HPO_4)_2H_2O$ $Zr(HPO_4)(H_2PO_4)(OH)$	-	Cs^+, Rb^+, K^+, Na^+ Cs^+, Pb^{2+}, Eu^{3+} Sr^{2+}, Co^{2+}, Ni^{2+} Zn^{2+}	83-93
		Semi Crystalline	-	-	-	Li^+, K^+, H^+, Cs^+	
		Crystalline	-	$Zr(HPO_4)_2.H_2O$	-	Sr^{2+}, UO_2^{2+}, Ce^{4+} Na^+, Cs^+	
2.	Zirconium Pyrophosphate	Amorphous	P/Zr=2.0,	-	-	Cu^{2+}, Ni^{2+}, Ca^{2+} Na^+, Fe^{2+}, Mg^{2+}	94-95
3.	Zirconium hypophosphate	Amorphous	Zr:P=1:1.75	-	-	For multivalent metals	96-98
4.	Zirconium polyphosphate	Amorphous	-	-	-	For Alkali metals in NH_4^+ form and Fe^{3+}, Cu^{2+}, Ca^{2+}, Ba^{2+} in H^+ form	99,101

Table 1 (Continued)

S.No.	Material	Type of Exchanger	Composition	Emperical formula	I.E.C.	Selectivity	Refs.
5.	Zirconium antimonate	Amorphous	-	-	-	Na^+,K^+,NH_4^+,Rb^+ Cs^+,Li^+	102-103
6.	Zirconium arsenate	Amorphous	As:Zr=1.53:1.96	-	-	Cs^+,K^+,Na^+ at p_H 2.6 Na^+,K^+ Cs^+ at p_H 4.6	104-105
		Crystalline	-	$Zr(HASO_4)_2 \cdot H_2O$	-	-	
7.	Zirconium molybdate	Amorphous	Zr:Mo=0.5:2.0	-	2.18 for K^+	-	106
8.	Zirconium tungstate	Amorphous	Zr:W=1.0 0.44	-	-	Cs^+,Rb^+,K^+, Na^+,Li^+	107-109
9.	Zirconium tellurate	Amorphous	-	$Zr(H_2TeO_6) \cdot 4H_2O$	2.8	-	110-111
10.	Zirconium Oxalate	Crystalline	-	$Zr(OH) \cdot C_2O_4H$	2.50	Na^+,Cs^+,Rb^+, K^+	112
11.	Zirconium Silicate	Amorphous	-	-	3.18	Th^{4+}, Sm^{3+},Ca^{2+} Sr^{2+}	113,114
12.	Zirconium ferrocyanide	Amorphous	Fe/Zr=0.55	-	.0.95	Li^+,Na^+,NH_4^+	115

Table 1 (Continued)

S.No.	Material	Type of Exchanger	Composition	Emperical formula	I.E.C.	Selectivity	Refs.
13.	Zirconium hydrogen phosphate pentahydrate	Crystalline	-	$[ZrNaH(PO_4)_2 \cdot 5H_2O]$	-	K^+, Cs^+, Na^+, Li^+	116
14.	Zirconium Silicomolybdate	Amorphous	-	-	-		168
II.	Thorium Satls						
15.	Thorium phosphate	Crystalline	-	$Th(HPO_4)_2 \cdot 3H_2O$	3.70	-	117
16.	Thorium arsenate	Crystalline	-	$Th(HASO_4)_2 \cdot H_2O$	-	-	118
17.	Thorium molybdate	Crystalline	-	-	0.75 at 100°C	$Fe^{3+}, Zr^{4+}, Pb^{2+}$	119
18.	Thorium tungstate	Amorphous	Th/W=2.0	$Th(OH)_2(HWO_4)_2 \cdot nH_2O$	0.46	Cs^+, K^+, Na^+	120
19.	Thorium tungstate	Crystalline	Th:W=1:6.2	-	-	Bi^{3+}, Hg^{2+}	121
20.	Thorium antimonate	-	Sb/Th=3.67,4.27 etc.	-	-	-	122
21.	Thorium tellurite	Amorphous		-	-	$Cu^{2+}, Pb^{2+}, VO_3^-, BrO_3^{3-}$	100

Table 1 (Continued)

S.No.	Material	Type of Exchanger	Composition	Emperical formula	I.E.C.	Selectivity	Refs.
III.	Titanium Salts						
22.	Titanium phosphate	Amorphous	P:Ti=0.6:2.0	$Ti_3(PO_4)_4$ $TiH_2(PO_4)_2 \cdot 4H_2O$	- 7.5	- Cs^+	123-130
23.	Titanium arsenate	Amorphous	-	$Ti(HASO_4)_2$ 2.5 H_2O	1.00	Pb^{2+}, Cu^{2+}, Ba^{2+} Sr^{2+}, Zn^{2+}, Cd^{2+}	131
24.	Titanium arsenate	Crystalline	-	$Ti(HASO_4)_2$ H_2O	5.80	-	132
25.	Titanium antimonate	Amorphous	Sb/Ti=1.0	-	0.70	Rare earth metals	133
26.	Titanium Selenite	Amorphous	Ti/Se=1.39	-	0.78	Cd^{2+}	134
27.	Titanium tellurite	Amorphous	Te/Ti=2.06	-	-	-	135,130
28.	Hydrous Titanium Oxide	Crystalline Fibres	-	TiO_2 $0.6H_2O$	-	$Cu^{2+} > Sr^{2+} > Zr^{4+}$ $Mn^{2+} > Co^{2+} > Ni^{2+}$	138
29.	Titanium (IV) antimonate	Amorphous	-	-	-	Li^+, K^+, Cs^+, Na^+, Rb^+	136
30.	Titanium phosphate	Amorphous	-	α-$Ti(HPO_4)_2H_2O$	-	Li^+	137

Table 1 (Continued)

S.No.	Material	Type of Exchanger	Composition	Emperical formula	I.E.C.	Selectivity	Refs.
IV.	Cerium IV Salts						
31.	Cerium phosphate	Amorphous Microcrystalline	P:Ce=1.03-1.95 P/Ce=1.5	$Ce_3(OH)_8(H_2PO_4)_4$ $(Ce-O-Ce)(HPO_4)_3$ H_2O	2.90 5.2	$Cs^+, Rb^+, K^+, Na^+, Li^+$ Cs^+, Na^+, Ag^+	139-145
32.	Cerium phosphate sulfate	Crystalline	Ce:P:S=2:1:2	$Ce_2O(HPO_4)_{3-x}(SO_4)_x \cdot 4H_2O$ where $0 < x < 1$	-	Na^+, Ag^+, Sr^{2+} Cs^+, Ca^{2+}	139
33.	Cerium (IV) arsenate	Microcrystalline	As/Ce=2.0	$Ce(HASO_4)_2 \cdot 2H_2O$	4.25	-	146
34.	Cerium antimonate	Amorphous	-		-	-	147
35.	Cerium molybdate	-	-	-	0.96	-	148
36.	Hydrous ceriumoxide	Crystalline	-	-	-	-	149
37.	Cerium selenite	Amorphous	Ce : Se = 1:1	$CeO_2 \cdot Se(OH)_2O \cdot n H_2O$	0.98	Hg^{2+}	151
38.	Cerium (IV) tellurite	-	-	-	0.90	-	152
39.	Ceric phosphate	Granular	Ce:PO_4 =1:2	-	-	$^{210}Bi, ^{210}Pb$ $^{90}Y, ^{90}Sr$	153

Table 1 (Continued)

S.No.	Material	Type of Exchanger	Composition	Emperical formula	I.E.C.	Selectivity	Refs.
40.	Cerium (IV) selenite	Amorphous	1:1			-	169
41.	Ceric tungstate	Amorphous	Ce:W = 1:1	-	-	Ca^{2+},Cu^{2+},Zn^{2+} Cd^{2+},Cr^{3+},Y^{3+}, Ce^{4+},Nd^{3+},Sm^{3+}, Tb^{3+},Tm^{3+},Yb^{3+}, Lu^{3+},Zr^{4+},Hf^{4+}, Sn^{4+},Nb^{5+},Se^{4+}, Mo^{6+} and W^{6+}	150
V.	Tin (IV) Salts						
42.	Stannic phosphate	Amorphous	P:Sn=1.25:1.50	-	1.20-1.44	Cs^{+},Rb^{+},K^{+}, Na^{+},Cu^{2+},Zn^{2+}, Ni^{2+},Co^{2+}	154
	Stannic phosphate	Crystalline	-	$Sn(HPO_4)_2^{\cdot}$ H_2O	7.90	-	
43.	Stannic arsenate	Amorphous	Sn/As=1.8	-	0.79-0.94	Al^{3+},Ga^{3+},In^{3+}	155-156
		Crystalline	-	$Sn(HASO_4)_2^{\cdot}$ H_2O	-	-	
44.	Stannic molybdate	Amorphous	Sn:Mo=1:1	-	1.0	Pb^{2+}	157

Table 1 (Continued)

S.No.	Material	Type of Exchanger	Composition	Emperical formula	I.E.C.	Selectivity	Refs.
45.	Stannic tungstate	Semitransparent	Sn/W=1.3	-	0.58	Co^{2+},Ba^{2+},Ni^{2+} Pb^{2+},Mn^{2+},Cu^{2+}, Sr^{2+}	158
46.	Stannic antimonate	Amorphous	Sb:Sn=1:1	-	0.75	Cu^{2+},Ni^{2+},Co^{2+}	159
47.	Stannic selenite	Amorphous	Sn/Se=1.33	$(SnO_4)(OH)_2$ $(SeO_3)_3.6H_2O$	0.75	Li^+,Na^+,K^+	160
48.	Stannic ferrocyanide	Amorphous	Sn/Fe=3.0	$[(SnO)_3(OH)_3$ $HFe(CN)_6.3H_2O]_n$	2.02	K^+,Ba^{2+},Na^+	161
49.	Stannic Vanadate	Amorphous	Sn/V=1.0	$[(Sn(OH)_3)_3$ $V_3O_9.4H_2O]_n$	0.85	K^+,Na^+,Li^+	162
50.	Stannic sulfide	Amorphous	-	-	0.20	Cu^{2+}	163
51.	Tin oxide (hydrated)	Amorphous	-	-	-	$Fe(CN)_6^{4+}$ SCN^-	164
52.	Stannic Pyrophosphate	Amorphous	-	-	-	Zr^{4+},Th^{4+} and Bi^{3+}	277
53.	Stannic Pyrophosphate and stannic selenophosphate	Amorphous	-	-	-	Th^{4+},Bi^{3+},Fe^{3+}	193

Table 1 (Continued)

S.No.	Material	Type of Exchanger	Composition	Emperical formula	I.E.C.	Selectivity	Refs.
VI.	Chromium Salts						
54.	Chromium phosphate	Amorphous (polyfunctional)	P:Cr=0.6:1.0	$Cr_2O_2HPO_4$ $Cr_2O(HPO_4)_2$	5.9	Na^+,K^+,Rb^+, Cs^+,Ca^{2+},Sr^{2+}, Ba^{2+}	165
55.	Chromium tripoly phosphate	Glassy	Cr:P=1:2.48	$Cr_5(P_3O_{10})_3 \cdot nH_2O$	-	Cs^+,Rb^+,K^+,Na^+ H^+	166
56.	Chromium arsenate	Amorphous	As/Cr=1.98	$Cr_2O_3 \cdot (H_3AsO_4)3H_2O$	0.63	Zr^{4+},Hf^{4+}	167
57.	Chromium molybdate	Amorphous	Mo/Cr=1.90	$Cr_2O_3(H_2MoO_4)_4 \cdot 8H_2O$	0.34	Pb^{2+},Ga^{3+}	167
58.	Chromium tungstate	Amorphous	W/Cr=1.92	$Cr_2O_3(H_2WO_4)_4 \cdot 11H_2O$	0.02	Th^{4+},Hf^{4+}	167
59.	Chromium antimonate	Amorphous	Sb/Cr=2.95	$Cr_2O_3.3Sb_2O_5 \cdot 22H_2O$	0.42	Pb^{2+},Co^{2+}	167
60.	Chromium tellurate	Amorphous	Te/Cr=0.2	-	-	-	135
61.	Chromium ferrocyanide	Amorphous	-	-	-	-	170

Table 1 (Continued)

S.No.	Material	Type of Exchanger	Composition	Emperical formula	I.E.C.	Selectivity	Refs.
VII.	Ferric (III) Salts						
62.	Ferric phosphate	Amorphous	P/Fe=2.0	$FeH(HPO_4)_2^{\cdot}$ nH_2O	0.77	Pb^{2+},Eu^{3+},Ga^{3+}	171
63.	Ferric arsenate	Amorphous	As/Fe=1.33	-	0.80	K^+,Na^+,Li^+	172
64.	Ferric ferrocyanide	Amorphous	-	-	3.60	Cs^+	75
65.	Ferric antimonate	Amorphous	Sb/Fe=2.4	-	0.82	Ca^{2+}	173
VIII.	Other Acid Salts						
66.	Tantalum antimonate	Amorphous	Ta/Sb=1.3	-	0.99	K^+,NH_4^+,Na^+	174
67.	Tantalum arsenate	Amorphous	Ta/As=2.8	-	1.09	Ba^{2+},K^+,Na^+	175
68.	Niobium arsenate	Amorphous	Nb/As=1.79	-	0.90	Ni^{2+},Mn^{2+}	176
69.	Niobium arsenate	Amorphous	Nb/As=1.96	-	1.06	Rare Earth Elements	177
70.	Niobium antimonate	Semicrystalline	Nb/Sb=1.41	-	1.10	Mg^{2+} selective	178
71.	Niobium molybdate	Semicrystalline	Nb/Mo=0.93	-	0.80	La^{3+}selective	179

Table 1 (Continued)

S.No.	Material	Type of Exchanger	Composition	Emperical formula	I.E.C.	Selectivity	Refs.
72.	Stannous ferrocyanide	Amorphous	Sn/Fe=1.0	$[SnO.H_4Fe(CN)_6 2.5H_2O]_n$	2.03	$Cu^{2+}, Ni^{2+}, Mn^{2+}$	180
73.	Molybdate ferrocyanide	Semicrystalline	Fe/Mo=2.3	$(H_4Fe(CN)_6)_4' (MoO_3(H_2O)_n)_{16}$	12.00	Cs^+	181
74.	Copper ferricyanide	Crystalline	-	-	-	$^{137}Cs^+$	182
75.	Lithium mangnate	Crystalline (Ion-Sieve)	-	$LiMnO_4$	1.8-1.9	Li^+	183
76.	Antimonic (V) acid	Crystalline	-	$Sb_2O_5.4H_2O$	1.28	K^+, Li^+	184
77.	Aluminium antimonate	-	-	-	-	$Mg^{2+}, Ba^{2+}, Hg^{2+}$ $Cd^{2+}, Zn^{2+}, Zr^{4+}$	186
78.	Aluminium vanadate	-	-	$(Al_2O_3)_n(V_2O_5)_m$ n:m=2.0-0.5	-	-	185
79.	Aluminium silicate	Amorphous	-	-	-	-	187
80.	Potassium alumino silicate	Crystalline	-	-	1.9	-	188
81.	Sodium alumino silicate	Crystalline	-	-	1.12	-	188

Table 1 (Continued)

S.No.	Material	Type of Exchanger	Composition	Emperical formula	I.E.C.	Selectivity	Refs.
82.	Uranyl hydrogen phosphate	-	-	$UO_2HPO_4 \cdot 4H_2O$	-	Cs^+, Rb^+, K^+	190
83.	Ammonium nickel phosphate	-	-	$(NH_4)_nNi_mPO_4 \cdot 6H_2O$ n=0.3-1.0, m=1.0-1.1	-	-	191
84.	Tungston ferrocyanide	Amorphous	W:Fe=1.32:1	-	1.02	-	192
85.	Tungston oxide	Amorphous	-	-	-	-	187
86.	Hydrous Tungston (IV) oxide	Amorphous	-	-	-	$Mg^{2+}, Ni^{2+}, Mn^{2+}$	194
87.	Bismuth Tungstate	Amorphous	Bi:W=1:1.99	-	0.52	Pb^{2+}, Ag^+	195
88.	Zinc ferrocyanide	Amorphous	Zn:Fe=1.98:1	$Zn_2Fe(CN)_6$	6.10	Cs^+	196
89.	Lead antimonate	Amorphous	Pb:Sb=1:5	$PbO.2.5Sb_2O_5$ $13H_2O$	1.46	Pb^{2+}, Cd^{2+}	197

Table 1 (Continued)

S.No.	Material	Type of Exchanger	Composition	Emperical formula	I.E.C.	Selectivity	Refs.
90.	Lanthanum tellurate	Amorphous	-	-	-	-	198
91.	Lanthanum antimonate	Amorphous	-	-	-	Hg^{2+}	199
92.	Lanthanum arsenate	Amorphous	La:As=1:1.4	-	0.87	Cu^{2+},Ni^{2+},Fe^{3+} Mn^{2+}	62
93.	Hafnium phosphate	Amorphous	-	-	-	-	200
94.	Hydrous magnese dioxide	Amorphous	-	-	-	K^{+},Rb^{+} and Ba^{2+}	189

For a complete description of a material as an ion-exchanger the following properties must be studied.

1. Ion exchange capacity
2. Resistance to acids and bases
3. Chemical composition
4. Potentiometric studies
5. Distribution of counter ions between the two immiscible phases (solution and exchanger)
6. Thermodynamics
7. Kinetics
8. Analytical Applications

Ion exchange capacity is one of the most fundamental parameters for the characterization of an ion exchange material. For strong ion exchangers simple titrimetric analysis is usually sufficient to determine ion exchange capacity. Various types of capacities can be determined in different manners. The equilibrium ion exchange capacity for strong ion exchangers can be determined by direct titration of strong cation exchangers (in H^+ from). Synthetic inorganic ion exchangers behave as weak ion exchangers and therefore, the direct titration method is not reliable. In such cases the ion-exchange capacity is determined by replacement of the hydrogen ions from the exchanger phase by counter ions of the neutral salt solution, and the equilibrium ion exchange capacity is determined by pH titrations.

The batch method is ideal for this purpose as this method allows equilibrium to be obtained, however the column method is more convenient and is satisfactory if the elution is carried out at a very slow rate.

The maximum ion exchange capacity, equal to the number of ionogenic groups per specified amount of the ion exchanger may be determined by the simple column operation in which the electrolyte solution is permeated over the ion exchange material.

There are other methods to determine the ion exchange capacity for solid ion exchangers for example the gravimetric method[201] which offers an advantage of high accuracy with extremely simple apparatus.

The resistance of ion exchangers to reasonable concentrations of acids and bases is important to check both its strengths and limitations.

The monofunctional or poly functional nature of the exchanger can be determined by direct potentiometric titrations. Alberti has studied such titration curves in detail on zirconium phosphate with alkaline metal hydroxides[202]. He observed that the curves are strongly affected by hydrolysis of the exchanger and by the precipitation of insoluble phosphates. He found that Ca^{2+} precipitates on the exchanger with 70% exchange, Sr^{2+} with 80% and Ba^{2+} with 100%. No exchange was observed with $Mg(OH)_2$. This probably is, due to the fact that large hydrated

ionic size of Mg^{2+} percludes it from the exchanger cavities. Alberti also studied the forward and reverse sodium-potassium exchange isotherms[203] on crystalline zirconium phosphate and found that the sodium-potassium exchange in aqueous solution is a two step process with a partial phase solubility. In the study of ion exchange behaviour on crystalline zirconium phosphate prepared either by refluxing or by direct precipitation, Alberti[204] observed that the two materials, exhibit different ion exchange properties, though each exhibits similar X-ray diffraction patterns.

Thermodynamics is a very important tool to study the theory of ion exchange and also for an insight to the underlying mechanisms involved.

Two different approaches are usually applied for this purpose (though other meritable approaches exist, these two are the most widely accepted).

The first approach is based on the design of more and more elaborate models. This approach gives a semiquantitative picture to a practical chemist who is interested in understanding the physical causes of the phenomena. The choice of the model, however, is crucial and the approach is restricted. The answer of course lies in thermodynamics. Thermodynamics is the appropriate means of explaining any equilibria. Rigorous thermodynamics, however, is, inherently abstract. The rigorous and abstract treatment of thermodynamics is 'correct' and universal,

but it yields a minimum of information about the physical causes of the phenomena to which it is applied.

In the second approach attempts have been made to correlate the activities with some measurable quantities with the thermodynamic equations. Some of the approaches of this kind may be mentioned. The earliest approaches were mainly based on semiemperical or emperical equations to fit experimental results. Probably the first quantitative formulation of ion exchange equilibria was made by Gans[205] using the law of mass action in its simplest form. This concept was extended by Kielland[206]. A similar choice of the general treatment was given by Gaines and Thomas[207]. The most acceptable model, however, is the semiquantitative one of Gregor which relates selectivity to hydrated ionic volumes.

Inorganic ion exchangers offer advantages for these studies because of their rigid structure, negligible swelling and swelling pressure and a differential selectivity. When an exchanger in (say) 'A' form, where 'A' is any counter ion is placed in a solution of counter ion 'B', there will be an equilibrium set up for the distribution of A and B between the exchanger and the solution phases according to their selectivity for the exchanger phase. The exchange process, at equilibrium, may then be designated by a general equation of the form:

$$\bar{A} + B(aq) \rightleftharpoons \bar{B} + A(aq) \quad \ldots \quad (1)$$

where the bars represent the ion in the exchanger phase.

For the sake of convenience the effect of the co-ions on the equilibria may be neglected. The thermodynamic equilibrium constant for the above reaction may be written as

$$K_a = \frac{\bar{a}_B \, a_A}{\bar{a}_A \, a_B} = \frac{[\bar{B}][A]}{[\bar{A}][B]} \times \frac{\gamma B \; fA}{\gamma A \; fB} \qquad \ldots\ldots \quad (2)$$

where γ represents activity coefficient in the exchanger phase and f, the activity coefficient in the solution phase.

The particular use of the thermodynamic equilibrium constant is made to find out the free energy changes of the ion exchange process, usually, by the expression:

$$\Delta F = - R \; T \; \ln K_a \qquad \ldots\ldots \quad (3)$$

The ionic activity is governed by a lowering of the free energy of the system. This gives the information about the preferential uptake of the counter ions by the exchanger. From the K_a values at different temperatures, the enthalpy changes in the system may be evaluated. The enthalpy change is directly related to the changes in the number and the strength of the bonds involved in the ion exchange reaction.

The ion exchange equilibria of Li^+, Na^+, K^+ and Cs^+ was studied by Larsen and Vissers[208] and Gal and Ruvarac[209], on amorphous zirconium phosphate, of various compositions. Such studies were extended to study the thermodynamics of the alkali metal ions on semicrystalline zirconium phosphate[210-215]. Studies of ion exchange equilibria on Cobalt (II) hexacyanoferrat

has been carried out by Ceramic and Adamvoic[216]. The thermodynamics for alkali and alkaline earth metal cations on ferric antimonate[217-218] and niobium arsenate[219] were made in our laboratories. Some of the equilibrium studies on different ion exchangers with various systems are given in Table 2.

Studies have also been carried out towards the thermodynamics of anion exchange on inorganic ion exchangers. The reversibility of the Br^- - NO_3^- exchange on hydrous zirconia was demonstrated by Kraus[233]. Ruvarac and Tartanj[234] studied the thermodynamics of Cl^- and SO_4^{2-} in NO_3^- form of hydrous zirconia at 25-80°C. Similar studies were also made for the exchange of $Cr_2O_7^{2-}$, CrO_4^{2-}, SO_4^{2-}, $S_2O_3^{2-}$ and MnO_4^- on zirconium-bis-triethylamine[235], at 30-60°C. The thermodynamic quantities (ΔF^o, ΔS^o and ΔH^o) have been calculated from the measurements of the thermodynamic equilibrium constant.

Table 2

Thermodynamic Studies On Various Ion Exchange Materials

S.No.	Ion Exchange Material	Systems studied	Various parameters	Reference
1.	Crystalline α-zirconium phosphate	Na^+/H^+, Cs^+/H^+ exchange	Phases formed during the exchange at equilibrium	220
2.	α-Zirconium phosphate	K^+/H^+	ΔG^o, ΔH^o and ΔS^o	221
3.	Crystalline zirconium phosphate	Cs^+/H^+, Rb^+/H^+	Forward and reverse isotherms x-ray diffractogram	222
4.	α-Zirconium phosphate	H^+/Na^+	K, ΔG, ΔH and ΔS	223
5.	Semicrystalline zirconium phosphate	Cs^+/H^+ and H^+/Cs^+	K	224
6.	α-Zirconium phosphate	Li^+/Cs^+, Na^+/Cs^+ and K^+/Cs^+	K, ΔG^o and ΔH^o	225
7.	Crystalline antimonic acid	H^+/Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Ca^{2+}	ln K, ΔG, ΔH and ΔS	226
8.	Crystalline antimonic acid	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}/H^+	Selectivity sequence, reversibility X-ray studies.	227
9.	Crystalline antimonic acid	Mg^{2+}, Sr^{2+}, Ca^{2+}, Ba^{2+} and Pb^{2+}/H^+	Kielland coefficient, $(\ln K_H^M)X_M \longrightarrow 0$	228

Table 2 (Continued)

S.No.	Ion Exchange Material	Systems studied	Various parameters	Reference
10.	Crystalline antimonic acid	NH_4^+/H^+, $CH_3NH_3^+/H^+$, $C_2H_5NH_3^+/H^+$, $(CH_3)_2NH^+/H^+$, iso-$C_3H_7NH_3^+/H^+$ and $(C_2H_5)_2NH^+/H^+$	ln K, ΔG, ΔH and ΔS	229
11.	Crystalline antimonic acid	H^+/Li^+, H^+/Na^+, H^+/K^+, H^+/Rb^+ and Na^+/Cs^+	ln K, ΔG and X-ray studies	230
12.	Ce(IV) phosphate	Li^+/H^+, Na^+/H^+, K^+/H^+	ΔH^o	231
13.	Ferriate, (natural zeolite)	Na^+, K^+, Rb^+, Cs^+, Ca^{2+} Sr^{2+}, Ba^{2+}, NH_4^+ and Ag^+		232

The thermodynamics of ion exchange is helpful in investigating the conditions at equilibrium, but it does not give any information about the mechanism of change from one state to the other and the time required thereon. The kinetics of ion exchange takes these factors into consideration.

The kinetics of simple homogeneous chemical reaction is governed by their differential rate of the reaction depending on the concentrations of the reactants.

$$AX + BY \longrightarrow \text{Products}$$

$$R = k.[X]^{A}.[Y]^{B}$$

where k is the rate constant and [X] and [Y] are the concentrations of the reacting species and A and B are their orders.

Ion exchange kinetics involves three types of processes.

1. Interdiffusion of counter ions in the adherent film, 'the film diffusion control'.
2. Interdiffusion of counter ions in the ion exchanger itself, 'the particle diffusion control'.
3. Chemical exchange reactions between two types of counter ions.

It is important to note that of all the studies on ion exchange kinetics which have appeared in the literature to date, none of them has been shown by chemical exchange reactions.

Nachod and Wood[236] made the first serious study on the kinetics of ion exchange. They studied the reaction rate with

which ions from solution are removed by the solid ion exchanger or conversely the rate at which the exchangeable ions are released from the exchanger. Boyd et al[237] have later on studied the kinetics of metal ions on resin beads, and have given an elaborate understanding about particle and film diffusion which are governed by ion exchange.

Costantino et al[238] have studied the self diffusion process of Na^+ and K^+ ions on microcrystals of $Zr(NaPO_4)_2 \cdot 3H_2O$ and $Zr(KPO_4)_2 \cdot 3H_2O$ and modified Ficks equation to take into account the non-uniformity of the particle size. The equation so obtained was employed in the study of self diffusion rate of Na^+ and K^+ ions on the above mentioned exchangers.

Kinetic studies on inorganic ion exchangers were made in our laboratories and kinetic studies on the exchange of the cations Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Y^{3+} and Th^{4+} were made on tantalum arsenate[239]. Similar studies were also made on iron antimonate[240], stannic arsenate[241] and Sodium Dickite[242]. Kinetic studies of the exchange of anions on zirconium-bis-triethylamine[243] have also been made. The distribution of an ion between the exchanger and solution phases can give a direct measure of their relative selectivities. Often, the ion exchanger takes up certain ions in preference to other counter ions present. This selectivity depends mainly on

1. The Donnan potential
2. Sieve action
3. Complex formation

Selectivity is a very important factor for the study of separations, on the basis of the distribution coefficients it is possible to predict the feasibility of separation of one ion over the other. The distribution coefficient of a counter ion (A) is defined as

$$Kd = \frac{\text{Amount of counter ion (A) in exchanger phase } g^{-1}}{\text{Amount of counter ion (A) in solution phase } ml^{-1}}$$

A general use of the distribution coefficient is made in the elution technique used in separations. The rate at which ions move in ion exchange chromatography is proportional to its linear distribution coefficient. The inorganic ion exchangers have found numerous important analytical applications, some of which are

1. Purification of substances on an industrial scale
2. Separation of ions from one another on small ion exchange columns.
3. Ion exchange paper chromatographic separations
4. Electrophoresis
5. Ion exchange for gas chromatography
6. Solid state separations
7. Specific spot tests
8. Use of ion exchange beads to locate the end point in titrations.

The preparation of ion exchange resins possessing gooc thermal and chemical stability has been perhaps an exclusive quest. The anion exchange resins usually, are prepared by introducing

an amino or ammonium as positive ionogenic group into a solid polystyrene divinylbenzene matrix through the well known Friedel-Crafts condensation. An inorganic ion exchanger can be prepared by introducing the amino group in hydrous oxides of tin or tetravalent metal ions. The amino group may also act as a chelating group to certain cations and hence such materials may be used in two ways.

(i) as an anion exchanger

(ii) as a chelating exchanger

A number of chelate ion exchangers have been synthesized to encourage the application of ion exchange to a broader range of separations and for the selective removal and recovery of certain metal ions. Complex formation in such type of exchangers is based, mainly, on N, S and O acting as the donor atoms for the formation of coordinate bonds. A donor atom must have a high electron density (preferably lone pair of electrons) and hence of a high electronegativity. Chelating ion exchangers with Nitrogen as the sole donor atom are relatively few, whereas chelating exchangers with both N and O as donor atoms are comparatively larger in number. Some of the important exchangers have been summarized in table 3.

Table 3

Some of the important ligand ion exchange resins

S.No.	Type of Exchanger	Sorption capacity m. mole/g	Selectivity	Refs.
1.	Oxime and diethylamino resin	2.00	Cu(II)	244
2.	8-hydroxyquinoline and 8-hydroxyquinodine resin	-	Cu(II), Zn(II)	245
3.	O-hydroxyoxime resin	-	Cu(II), Mo(VI)	246
4.	Thioglycolate resin	-	Ag(I), Bi(III), Sn(IV), Sb(III), Hg(II), U(VI) from pH = 3.5	247
5.	Aminoacid type resin	-	U(VI), Cu(II), Ni(II), Fe(III)	248
6.	Phosphate type resin	-	U(VI), Th(IV)	248
7.	N-Acylphenyl hydroxylamines	0.45	-	249
8.	Aluminium oxide	-	NH_4^+	250
9.	Alumina and silica gel	-	Ag(I)	251
10.	Microreticular resin	-	Ag(I)	252
11.	Cellulosic exchanger	-	Sb(III), Co(II)	253
12.	Cation exchange resin	-	Zn(II)	253
13.	Sulphonated type resin	-	Ni(II)	254
14.	Carboxylic ion exchanger	-	$Co(en)_3^{3+}$	255
15.	Chilosan	-	Cu(II)	256
16.	Chelating resin (Dithiocarbamate)	-	Cu(II)	257
17.	Acrylic resin	-	Cu(II)	258

Table 3 (Continued)

S.No.	Type of Exchanger	Sorption capacity m. mole/g	Selectivity	Refs.
18.	Chelating resin (Semithiocarbazide)	-	Pb(II) ,Pt(IV), Rh(III),Ir(III)	259
19.	Chelating resin poly(Vinylbezylthiourea)	819 mg/g	Au(III)	260
20.	Chelating resin poly(hydroxamic acid)	-	Cu(II),Cd(II), Zn(II)	261
21.	Chelating resin	-	Mo(VI),W(VI) U(VI),V(V)	262
22.	Chelating resin	1.9	Cu(II)	263

In addition to the materials mentioned so far, a number of other types of exchangers have been developed, for example, the electron and redox ion exchangers. The electron ion-exchangers may be considered as solid oxidation and reducing agents. They contain the species forming a redox couple and after having been oxidized (or reduced) by a substarate, the electron ion exchanger can be regenerated by a suitable reducing (oxidizing) agent. The activity of electron ion-exchanger is due to the built in redox components. The most important advantage of these materials over dissolved oxidizing (or reducing) agents is their insolubility, hence electron ion exchangers can easily be separated from the solution containing the substrate being oxidized (or reduced). The solution is free from the contamination of any redox agent on its products.

Only electrons and protons are transferred between the exchanger and the solution phase. Therefore, the only, possible change in solution, except for the redox reaction of the substrate, is a change in pH. Another advantage is that they can be readily regenerated (i.e. oxidized or reduced) after use.

The electron ion exchangers are characterized by their redox capacity, redox potential and reaction rate. The reaction rate indicates the time required for a redox process under a given set of conditions.

The Redox ion exchangers are conventional ion exchangers which contain reversible redox couples. The redox couples are introduced in the exchanger as counter ions. Some of the important redox exchangers are given in table 4.

Table 4

Redox ion exchangers and their redox capacity

S.No.	Name of Redox exchanger	Redox capacity (meq/g)	References
1.	Zirconiumphospho Iodate	-	264
2.	Hydrazine sulfate sorbed Zinc silicate	-	265
3.	Polystyrene based redox resin	-	266
4.	Phosphinic acid type redox resin	-	266
5.	Phosphomolybdovanadic acid	0.318	267
6.	Tetrachlorohydroquenione	-	268
7.	Tetrachloroquinone	-	269
8.	P- benzoquinone melomine copolymer	4.00	270
9.	Zirconium molybdovanadate	0.520	271
10.	Alkali and nikle ferrocyanide	-	272
11.	Phosphotungstovanadic acid	-	273
12.	Active carbon	-	274
13.	Zeolite alumino silicate	-	275
14.	Zirconium peroxidemetatungstate	-	276

In conclusion various chemical and physical studies have been carried out on ion exchange materials and their applicability to some systems has also been highlighted.

Detailed thermodynamic studies have been carried out on thoriumtetracyclohexylamine exchanger. Kinetic studies have also been carried out on the above exchanger and the mechanism of exchange elucidated. Some of the important separations have been achieved on the column of the above mentioned exchanger. An electron ion exchanger molybdenum-benzoinoximate was synthesized and the redox studies along with detailed structural studies were carried out and the structure was established by variety of modern techniques. An elagent method is described for the recovery of silver from laboratory wastes by a very simple procedure using ion exchange combined with ion exclusion.

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C H A P T E R - II

ANION EXCHANGE AND LIGAND EXCHANGE STUDIES ON THORIUMTETRACYCLOHEXYLAMINE

A number of inorganic ion exchangers have been synthesized by many workers[1-3] mainly for analytical separations. New materials have been synthesized for various specific problems. The use of amines for synthesizing inorganic based ion exchanging materials have been emphasized[4-5]. These materials serve in two ways (i) as anion exchangers by holding a positive charge on amino-nitrogen, (ii) as a complexing agent by the presence of lone pair of electrons on nitrogen, keeping this view, we have synthesized an ion exchange material by the combination of thorium nitrate and cyclohexylamine. Besides the studies on ion exchange behaviour and physical characterization, the thermodynamic studies have also been made to understand the feasibility of ion exchange.

Several theories for ion exchange equilibria have been developed and tried on inorganic ion exchangers[6-7]. Only few studies have been made about the anion exchange equilibria[8] This chapter describes the influence of temperature on the equilibria of SCN^- - NO_3^- , Cl^- - NO_3^- , MnO_4^- - NO_3^- and CrO_4^{2-} - NO_3^- exchange on thoriumtetracylohexylamine at constant ionic strength of 0.10 within the temperature range from 30-60°C, the thermodynamic parameters are calculated.

EXPERIMENTAL

Apparatus: An electric temperature controlled shaker, Bausch and Lomb Spectronic-20 (U.S.A.) and Elico p_H-meter model Li-10 (India) were used for shaking, spectrophotometric determinations and p_H measurements respectively.

Reagents: Thorium nitrate (Fissions, U.S.A.) cyclohexylamine (B.D.H. England) were used. The other chemicals used were of analytical grade.

Synthesis: The thoriumtetracyclohexylamine exchanger was prepared by mixing 0.10 M solutions of thorium nitrate and cyclohexylamine in the volume ratios of 1:1, 1:2, 1:3, 2:1 and 1:4 (Table 5). The precipitate thus obtained was kept standing for 24 h at room temperature (25 $\pm$ 1°C) to ensure complete precipitation. The precipitate was filtered and washed with deionized water. It was dried in an air oven at 40°C. The dried material was then broken in small particles simply by shaking in deionized water. The exchanger granules (50-100 mesh size) were converted in nitrate form by shaking in 2M solution of potassium nitrate. It was finally washed and dried at 40°C.

RESULTS

Table 5

Conditions of preparation of thoriumtetracyclohexylamine

S.No.	Conditions of Synthesis Molarity of reagents		Mixing ratio	Properties
	Thorium-nitrate (M)	Cyclohexylamine (M)		
1.	0.10	0.10	1:1	No precipitation
2.	0.10	0.10	2:1	No precipitation
3.	0.10	0.10	1:2	Mild precipitation
4.	0.10	0.10	1:3	Mild precipitation
5.	0.10	0.10	1:4	Thick precipitation

Anion exchange capacity:

The anion exchange capacitv of some uni and bivalent anions reported in table 6 were measured by column method. 2 M solution of potassium nitrate was used as eluting agent for SCN^-, Cl^-, Br^- and I^- while for CrO_4^{2-} and MnO_4^- 0.10 M solution of sodium hydroxide was used.

Table 6

Ion exchange capacity of thoriumtetracyclohexylamine for various anions at different temperatures

S.No.	Anions	Salt used	Capacity meq/g Temperature		
			40°C	60°C	80°C
1.	CrO_4^{2-}	K_2CrO_4	1.10	1.14	1.14
2.	SO_4^{2-}	K_2SO_4	1.08	1.10	1.10
3.	MnO_4^-	$KMnO_4$	1.02	1.06	1.06
4.	Cl^-	KCl	0.82	0.87	0.87
5.	Br^-	KBr	0.76	0.79	0.79
6.	I^-	KI	0.72	0.74	0.74
7.	SCN^-	KSCN	0.66	0.79	0.79
8.*	Cu^{2+}	$Cu(NO_3)_2$	0.52		
9.*	Ni^{2+}	$Ni(NO_3)_2$	0.69		

*Shows the sorption capacity

Chemical stability:

The chemical stability of all the samples were studied in different solvents, for this purpose 0.500 g of the exchanger was shaken with 25 ml solution of interest for 6 h at room temperature. The amount of thorium in the supernatant liquid was determined by titrating a known volume of solution against 0.01 M EDTA and the cyclohexylamine was determined spectrophotometrically in an other sample. The result are given in table 7.

Table 7

Chemical stability of thoriumtetracyclohexylamine in different solvents

Contacting solution	ppm found after contact test	
	Thorium	Cyclohexylamine
De-ionized water	0	0
2.0M Sodium nitrate	0	0
2.0M Sodium hydroxide	0	0
2.0M Hydrochloric acid	39.2	102.4
0.5M Hydrochloric acid	1.2	3.2
0.01M Hydrochloric acid	0	0
0.5M Sulphuric acid	4.8	59.6
0.5M Nitric acid	2.8	5.2
0.5M Perchloric acid	2.0	2.4
0.5M Acetic acid	0.4	1.6

Thermal stability:

In order to check the thermal stability, 0.500 g of the exchanger was heated in a muffel furnace at different temperatures ranging from 30-300°C and their capacities were measured. The results are given in table 8 and plotted in figure 2.

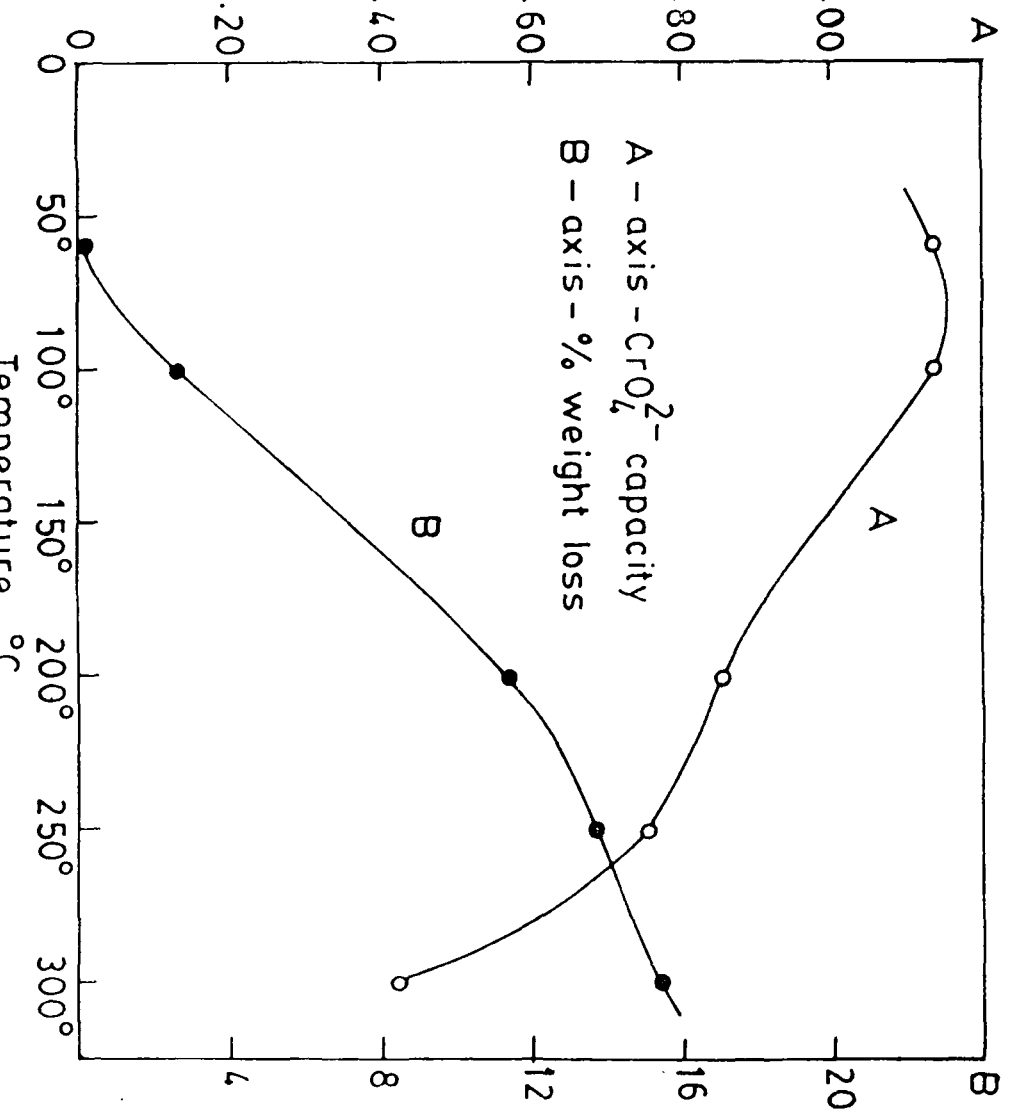


Fig.2 Capacity and % weight losses of exchanger at different temperatures.

Table 8

Capacity and weight losses of the exchanger at different temperatures

S.No.	Temperature (°C)	Weight taken (g)	Weight left (g)	Capacity for CrO_4^{2-} (meg/g)
1.	45	1.0000	1.0000	1.10
2.	60	1.0000	1.0000	1.14
3.	100	1.0000	0.9738	1.14
4.	200	1.0000	0.8864	0.84
5.	250	1.0000	0.8674	0.76
6.	300	1.0000	0.8462	0.42

Chemical composition:

For the determination of thorium 0.500 g of the exchanger was dissolved in 5 ml of 70% perchloric acid by heating on water bath and diluted to 50 ml with distilled water. Thorium in this sample was determined by titrating with 0.01 M solution of EDTA. For the determination of amine, 0.500 g of the exchanger was again dissolved in 5 ml of 70% perchloric acid, amine in this sample was determined spectrophotometrically using 4-dimethylaminobenzaldehyde at 440 nm.

p_H-titrations:

The added salt method[9] was used for pH titrations using NaCl-HCl system. For this purpose 0.500 g exchanger in OH^- form was taken. The results are plotted in figure 1.

Hydrolysis studies:

For hydrolysis studies, 0.500 g of the exchanger was shaken with distilled water for different time intervals viz. 5, 10, 20, 30, 40, 60, 80, 120 and 180 minutes. The pH of the solution was noted after each time interval. The results are given in table 9.

Table 9

Hydrolysis of thoriumtetracyclohexylamine at different time intervals

S.No.	Time (minutes)	pH
	Initial p_H of distilled water = 6.8	
1.	5	6.5
2.	10	6.2
3.	20	5.8
4.	30	5.3
5.	40	4.4
6.	50	4.3
7.	60	4.3
8.	90	4.3
9.	120	4.3
10.	180	4.3
11.	Over night	4.3

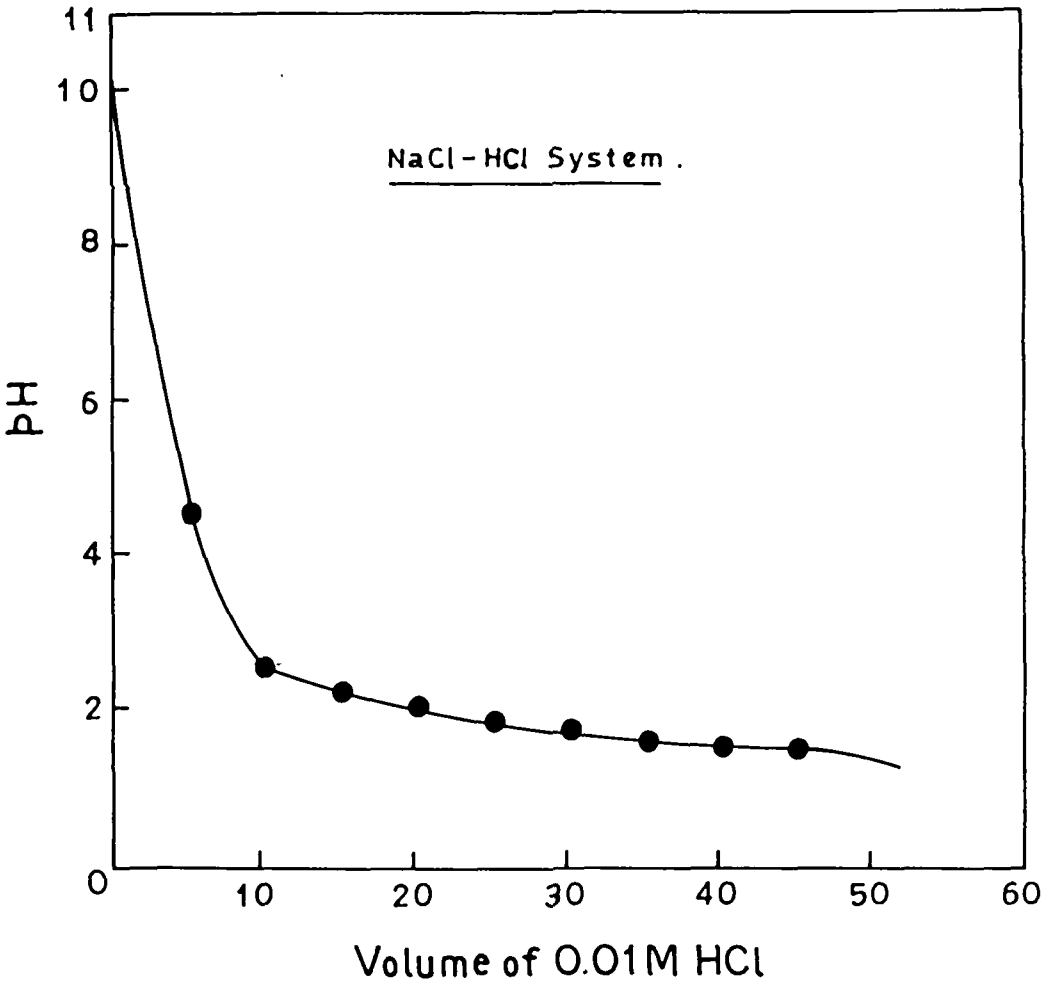


Fig.1- pH titration curve for thoriumtetracyclohexy- lamine .

IR-analysis:

The IR-spectrum of the material dried at 40°C was obtained using standard KBr disc technique (figure 3 and 3a).

Distribution coefficient:

Values of distribution coefficient for various anions were determined by batch process. 1 ml of anionic solution was taken in 50 ml volumetric flask, the remaining volume was filled up with the solution in which its distribution coefficients were to be studied. This solution was then shaken with 0.500 g of the exchanger for 6h in a shaker. The supernatant liquid was then titrated for the determination of anions left. Results of Kd values in de-ionized water and in different solutions of sodium hydroxide are given in table 10.

Table 10

Distribution coefficient values for different anions in different solvents

S.No.	Anions	Kd/mlg^{-1}			
		H_2O	NaOH (10^{-4}M)	NaOH (10^{-3}M)	NaOH (10^{-2}M)
1.	Bromide	90.00	83.00	56.00	24.00
2.	Bromate	176.00	157.00	96.54	39.10
3.	Chloride	80.00	69.30	57.61	26.63
4.	Chromate	560.00	349.00	254.30	107.50
5.	Dichromate	720.00	560.00	166.20	98.00
6.	Iodate	149.50	126.70	83.30	34.45

Table 10 (Continued)

S.No.	Anions	Kd/mlg^{-1}			
		H_2O	NaOH (10^{-4}M)	NaOH (10^{-3}M)	NaOH (10^{-2}M)
7.	Iodide	175.10	145.63	80.66	19.26
8.	Thiocyanate	160.82	103.54	86.98	37.64
9.	Peroxodisulfate	235.80	195.30	130.00	75.60
10.	Permanganate	520.00	320.00	225.00	75.00

Separations:

In order to develop the analytical utility of the exchanger various important separations were performed. For this purpose 3.00 g of the exchanger in nitrate form was taken in a glass column with a glass wool support. The mixture containing anions to be separated were applied from the top of the column and elution was made with an appropriate eluent. Several fractions of eluent were collected at a flow rate of 0.5 ml/minute and the anions in the eluent were then determined by standard methods. The successful binary separations are given in table 11 and the results are plotted in figures 4-6.

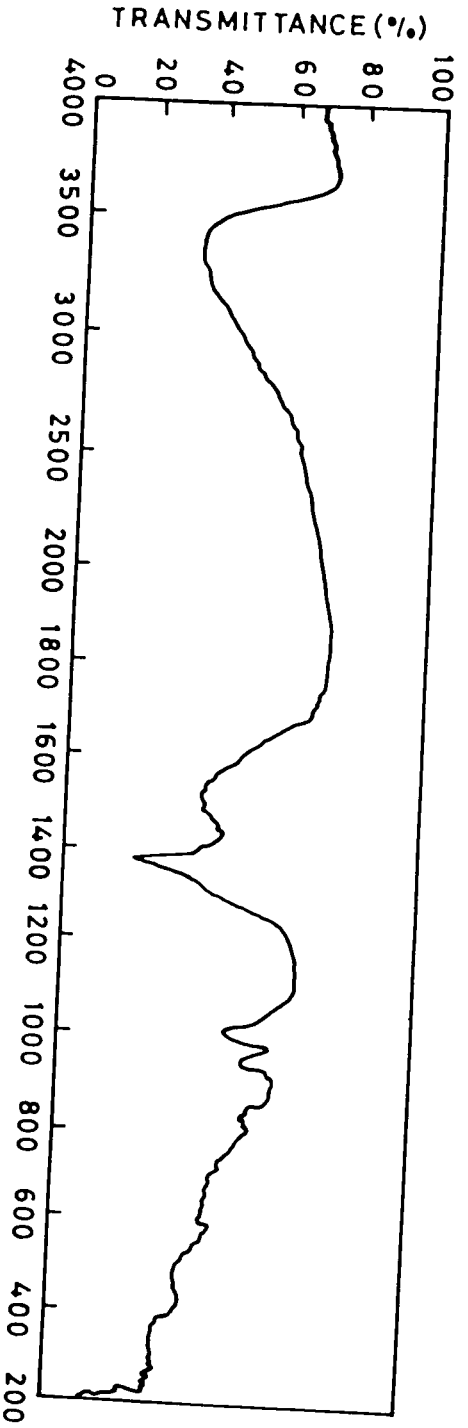


FIG.3_ IR SPECTRUM OF THORIUMTETRACYCLOHEXYLAMINE EXCHANGER.

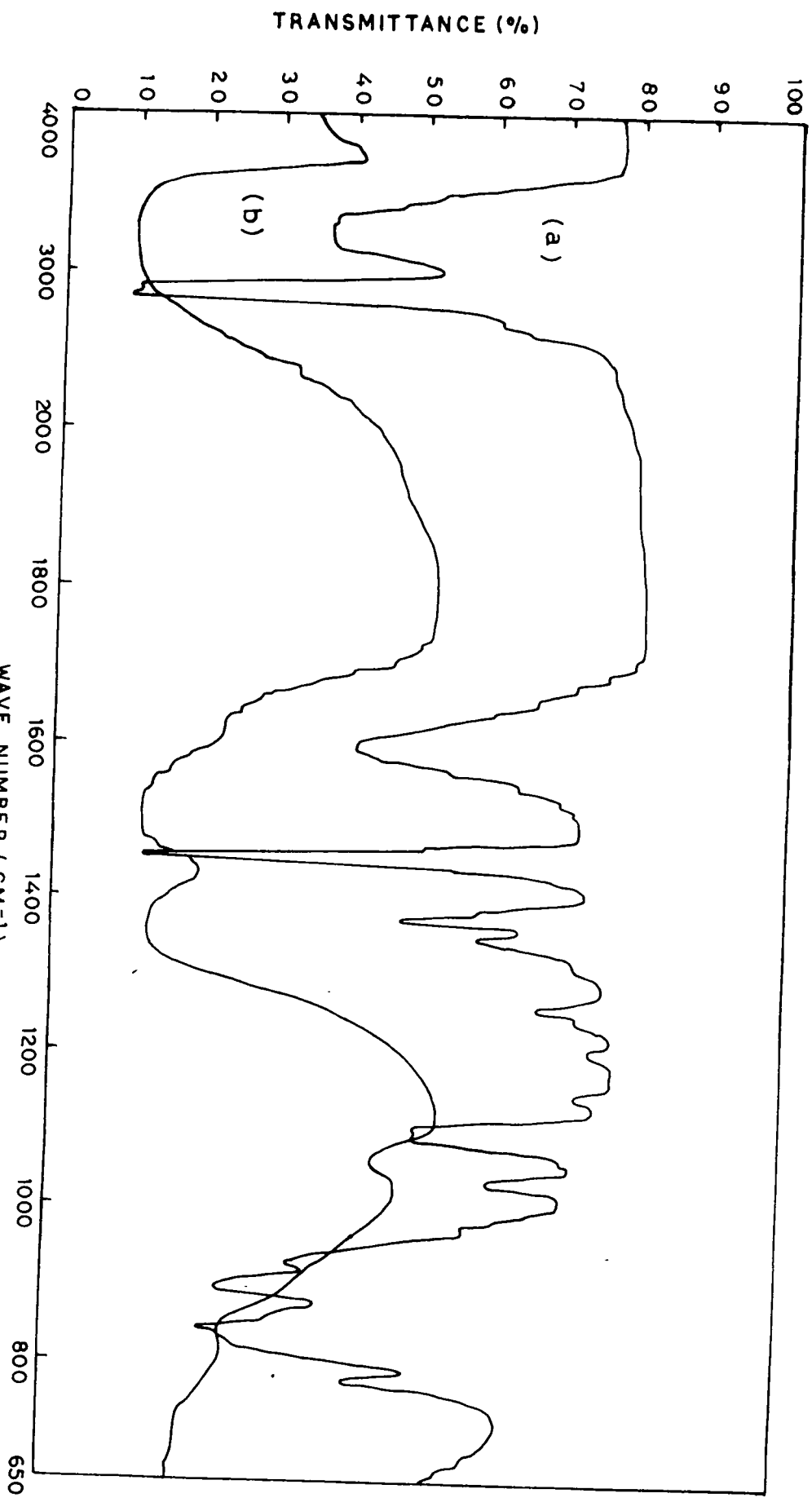


FIG:3: A (a) IR Spectrum of cychohexylamine
(b) IR Spectrum of exchanger in Cl- from

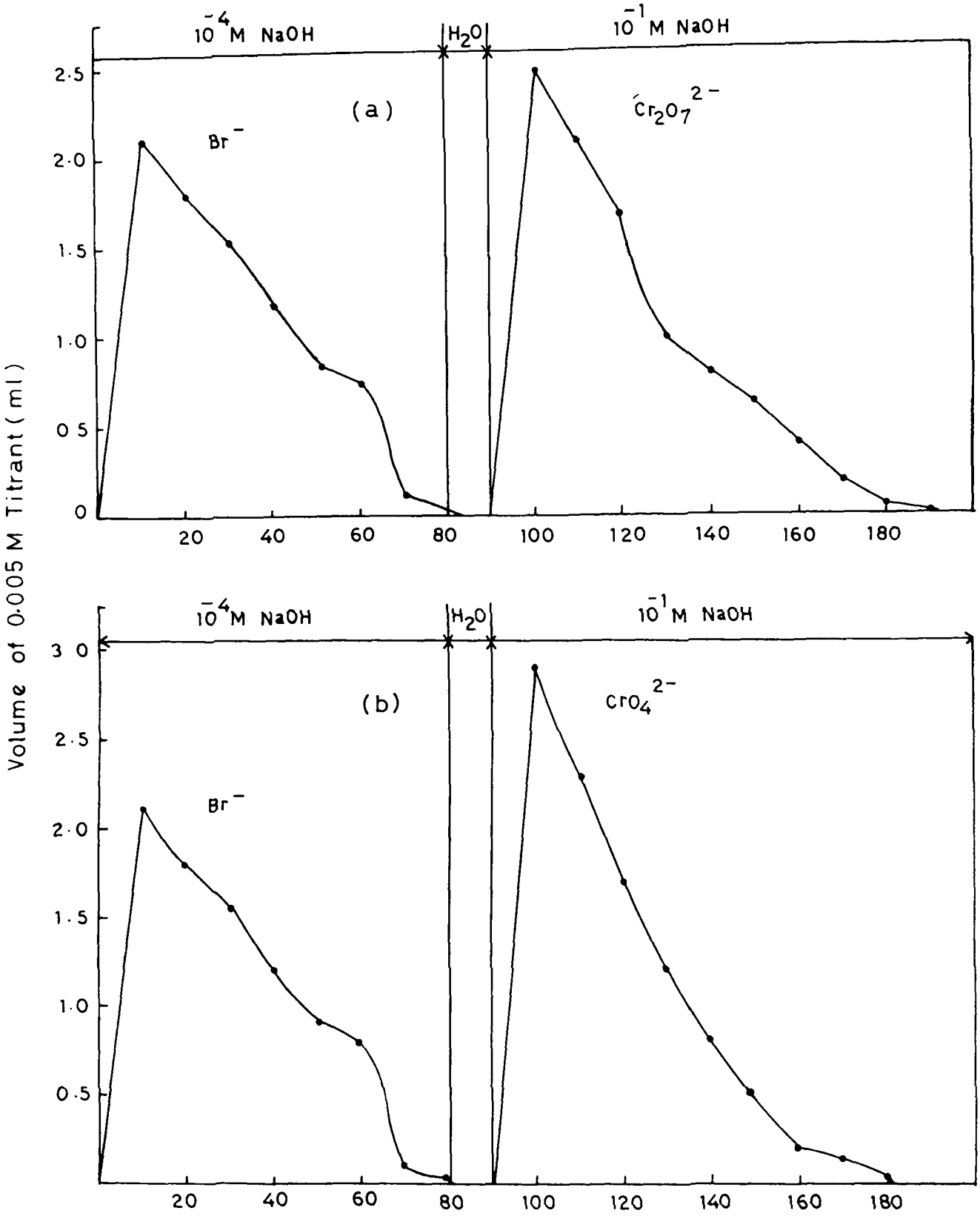


Fig 4 (a) Separation of Br^- from $Cr_2O_7^{2-}$

(b) Separation of Br^- from CrO_4^{2-}

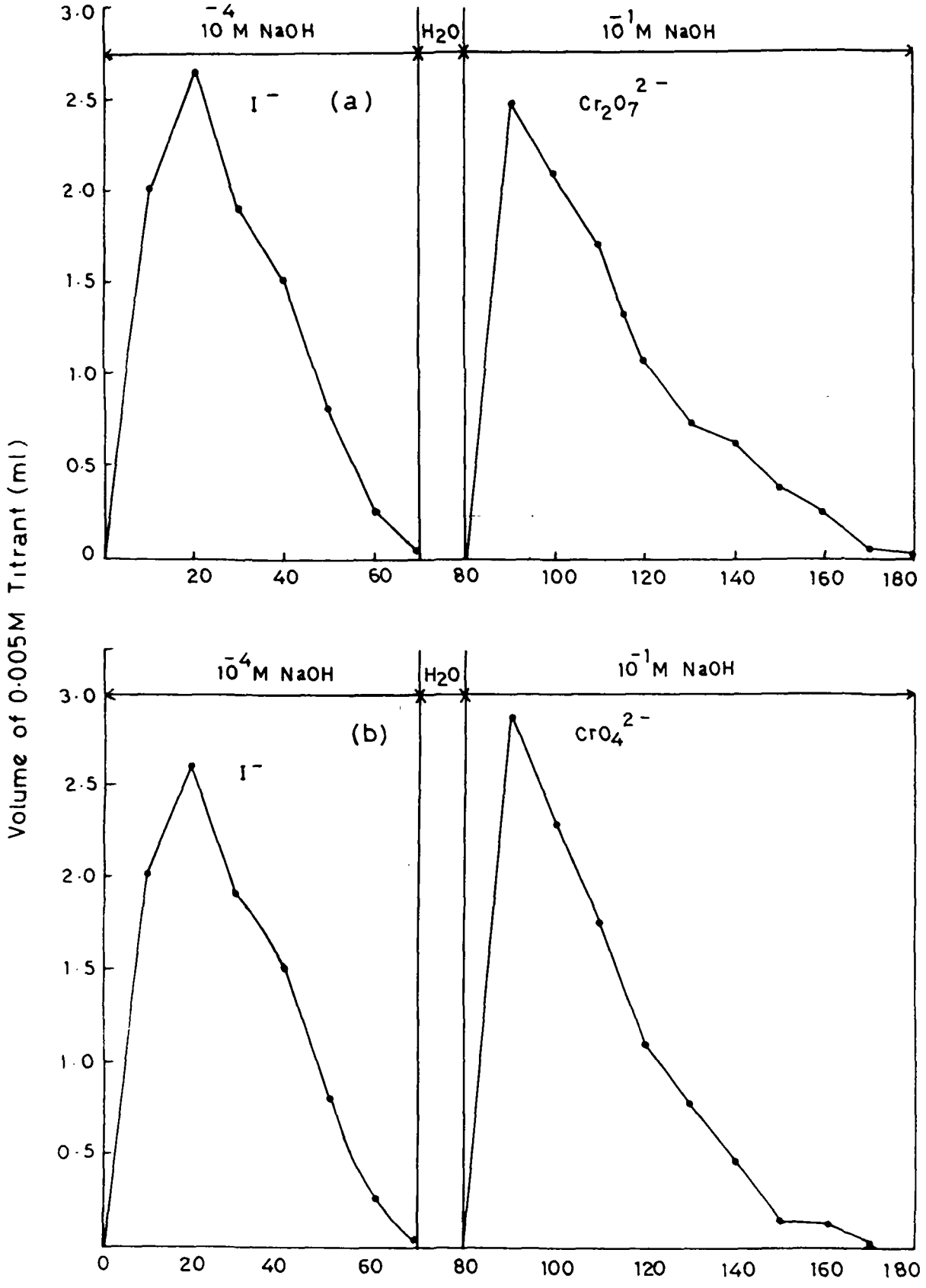


Fig: 5 (a) Separation of I^- from $Cr_2O_7^{2-}$

(b) Separation of I^- from CrO_4^{2-}

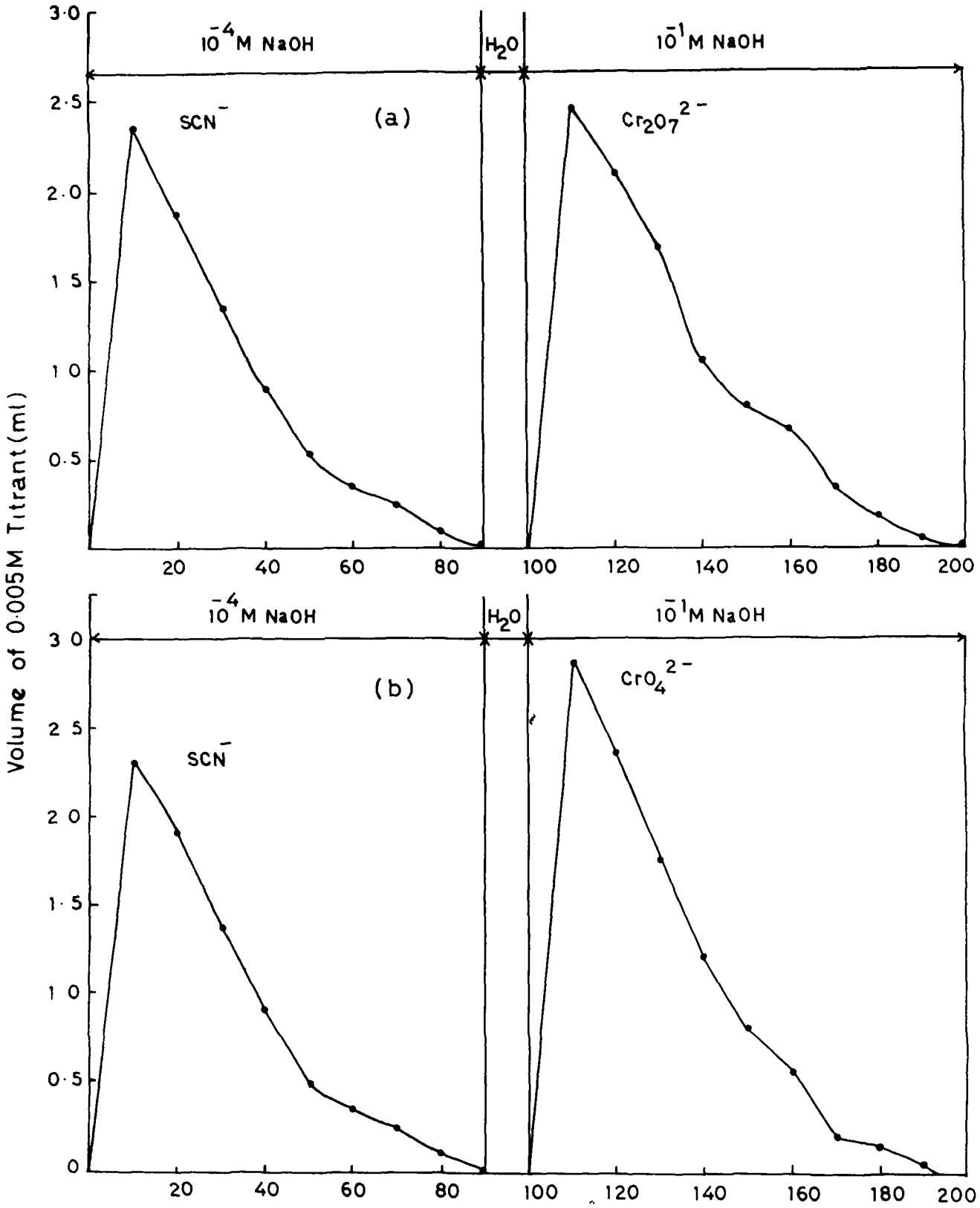


Fig 6 (a) Separation of SCN^- from $Cr_2O_7^{2-}$

(b) Separation of SCN^- from CrO_4^{2-}

Table 11

Quantitative separations of anions on thoriumtetracyclohexylamine

S.No.	Mixture	Eluent	Eluent (ml)	Amount loaded (mg)	Amount found (mg)	% Error
1.	Br^-	10^{-4}M NaOH	80	3.32	3.28	1.30
	CrO_4^{2-}	10^{-1}M NaOH	90	5.80	5.68	2.00
2.	Br^-	10^{-4}M NaOH	80	3.32	3.27	1.37
	$Cr_2O_7^{2-}$	10^{-1}M NaOH	100	10.37	10.18	1.77
3.	I^-	10^{-4}M NaOH	70	5.84	5.77	1.19
	CrO_4^{2-}	10^{-1}M NaOH	90	5.80	5.69	1.84
4.	I^-	10^{-4}M NaOH	70	5.84	5.76	1.38
	$Cr_2O_7^{2-}$	10^{-1}M NaOH	100	10.37	10.19	1.75
5.	SCN^-	10^{-4}M NaOH	90	2.32	2.25	1.74
	CrO_4^{2-}	10^{-1}M NaOH	90	5.80	5.69	1.80
6.	SCN^-	10^{-4}M NaOH	90	2.32	2.28	1.74
	$Cr_2O_7^{2-}$	10^{-1}M NaOH	100	10.37	10.18	1.84

The equilibrium experiments were performed by taking 20 ml solution containing potassium nitrate and appropriate anionic solution having constant ionic strength of 0.10. To this 0.500 g of the exchanger in nitrate form was added and the flasks were shaken for 6 h. in a temperature controlled shaker at desired temperature.

Reversibility experiments were performed by equilibrating the exchanger in a particular anionic form with a nion and potassium nitrate solution at 30°C. The exchange isotherms for various anions are plotted in figures 7-10 and the results of equivalent fractions, selectivity coefficients and equilibrium constant are given in tables 12-15.

Table 12

Equivalent fractions of SCN^-, selectivity coefficients and thermodynamic equilibrium constant for SCN^--NO_3^- exchange on thoriumtetracyclohexylamine

X $\bar{SCN}$	$\bar{X}$ SCN^-	Kc	Ka
(a) SCN^- - NO_3^- at 30 ± 1°C			
0.9176	0.5491	0.0897	
0.8676	0.2685	0.1526	
0.7903	0.1601	0.2644	
0.6983	0.1379	0.4320	
0.6065	0.1036	0.6486	0.355
0.5133	0.0667	0.9480	
0.4165	0.0415	1.4009	
0.3168	0.0222	2.156	
0.2133	0.0148	3.688	
0.1087	0.00145	8.202	

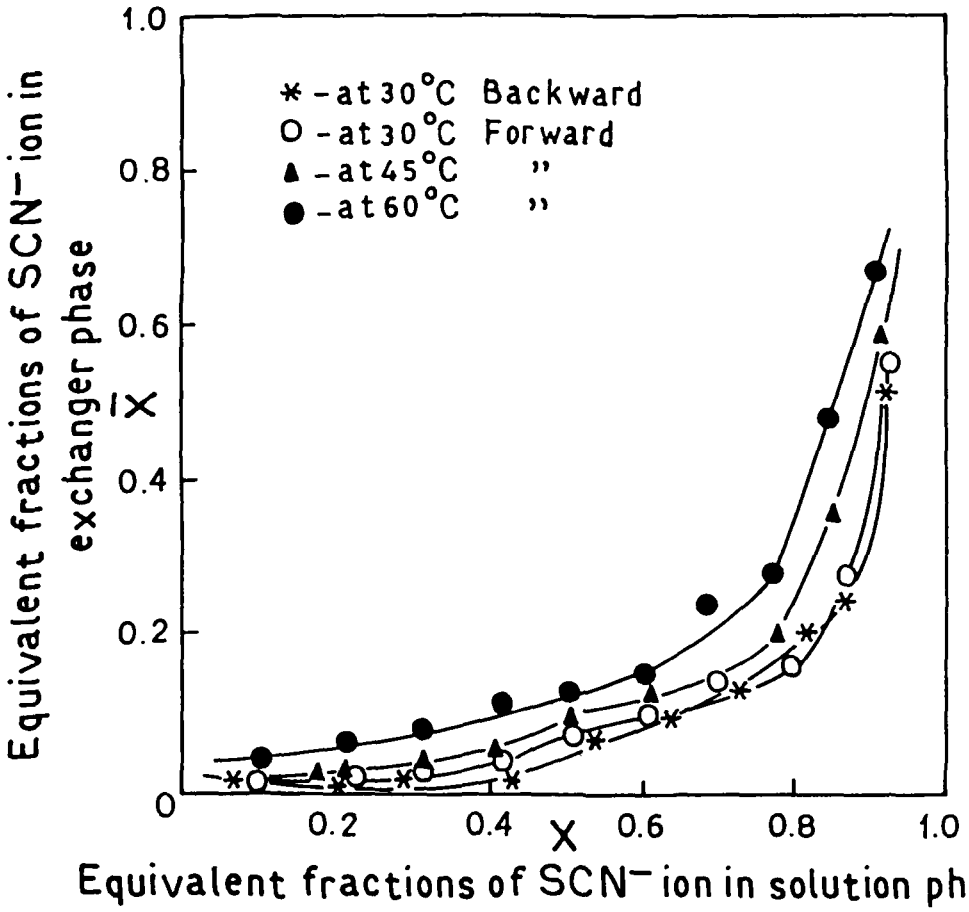


Fig. 7 – Ion exchange isotherm of SCN^- ion on thorium – tetracyclohexylamine.

Table 12 (Continued)

X SCN^-	$\bar{X}$ SCN^-	Kc	Ka
(b) $SCN^- - NO_3^-$ at 45 ± 1°C			
0.9132	0.5788	0.095	
0.8541	0.3576	0.1708	
0.7849	0.1958	0.2740	
0.6961	0.1527	0.4366	
0.6056	0.1097	0.6513	
0.5087	0.0964	0.9569	0.267
0.4146	0.0533	1.4119	
0.3164	0.0252	2.1607	
0.2103	0.0207	3.7117	
0.1673	0.0133	8.3691	
(c) $SCN^- - NO_3^-$ at 60 ± 1°C			
0.8998	0.6679	0.1113	
0.8362	0.4764	0.1960	
0.7713	0.2848	0.2965	
0.6823	0.2418	0.4655	
0.5986	0.1542	0.6705	0.21
0.5040	0.1261	0.9841	
0.4052	0.1127	1.4680	
0.3077	0.0786	2.2490	
0.2066	0.0564	3.8410	
0.1019	0.0430	8.8150	

Table 13

Equivalent fractions of Cl^-, selectivity coefficients and thermodynamic equilibrium constants for $Cl^- - NO_3^-$ exchange on thoriumtetracyclohexylamine

XCl^-	$\bar{X}Cl^-$	Kc	Ka
	$Cl^- - NO_3^-$ at 30 ± 1°C		
0.8600	0.6829	0.1628	
0.7980	0.5098	0.2531	
0.7220	0.3805	0.3850	
0.6345	0.3195	0.5760	0.14
0.5480	0.2537	0.8248	
0.4545	0.2220	1.2002	
0.3665	0.1634	1.7285	
0.2765	0.1146	2.6170	
0.1860	0.683	4.1380	
0.0955	0.0220	9.4713	
	$Cl^- - NO_3^-$ at 45 ± 1°C		
0.8545	0.7098	0.1703	
0.7920	0.5268	0.2626	
0.7190	0.3951	0.3908	
0.6305	0.3390	0.5860	0.11
0.5425	0.2865	0.8433	
0.4500	0.2439	1.2220	
0.3625	0.1829	1.7586	
0.2740	0.1268	2.6496	
0.1825	0.0854	4.4790	
0.0930	0.0341	9.943	

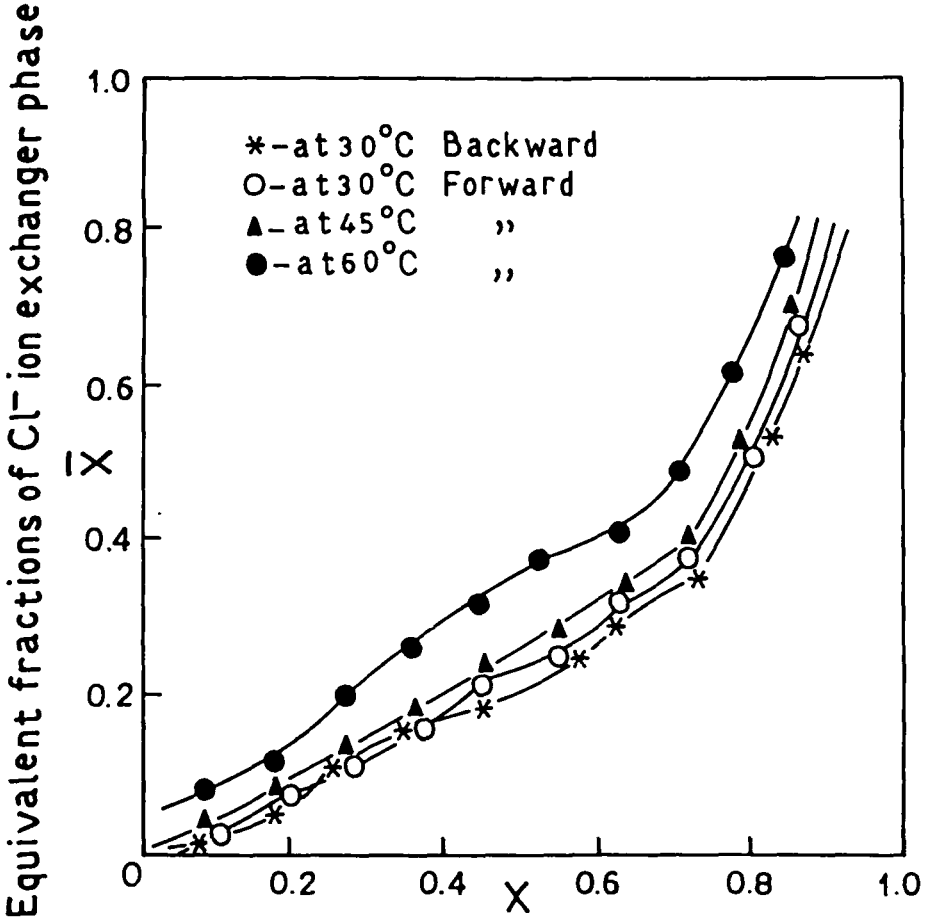


Fig: 8- Ion exchange isotherm of Cl^- ion on thorium-tetracyclohexylamine.

Table 13 (Continued)

XCl^-	$\bar{X}Cl^-$	Kc	Ka
	$Cl^- - NO_3^-$ at 60 ± 1°C		
0.8425	0.7683	0.1869	
0.7720	0.6244	0.2955	
0.6990	0.4927	0.4838	
0.6160	0.4098	0.6234	
0.5225	0.3780	0.9137	0.073
0.4350	0.3171	1.2990	
0.3470	0.2585	1.8818	
0.2590	0.2000	2.8610	
0.1675	0.1585	4.9762	
0.0830	0.08293	11.0480	

Table 14

Equivalent fractions of MnO_4^-, selectivity coefficients and thermodynamic equilibrium constants for $MnO_4^- - NO_3^-$ exchange on thoriumtetracyclohexylamine

X MnO_4^-	$\bar{X}$ MnO_4^-	Kc	Ka
	$MnO_4^- - NO_3^-$ at 30 ± 1°C		
0.6865	0.8831	0.4567	
0.6560	0.6873	0.5244	
0.6055	0.5479	0.6515	
0.5460	0.4338	0.8315	0.052
0.4825	0.3310	1.0725	
0.4105	0.2521	1.4366	
0.3310	0.1944	2.0211	
0.2250	0.1268	2.9220	
0.1730	0.07606	4.7803	
0.0830	0.0479	11.0500	
	$MnO_4^- - NO_3^-$ at 45 ± 1°C		
0.6810	0.8986	0.4684	
0.6510	0.7014	0.5361	
0.6025	0.5563	0.6598	
0.5405	0.4493	0.8503	
0.4775	0.3451	1.0940	0.047
0.4050	0.2676	1.4691	
0.3255	0.2099	2.0722	
0.2500	0.1408	3.0000	
0.1680	0.0901	4.9520	
0.0785	0.0606	11.7390	

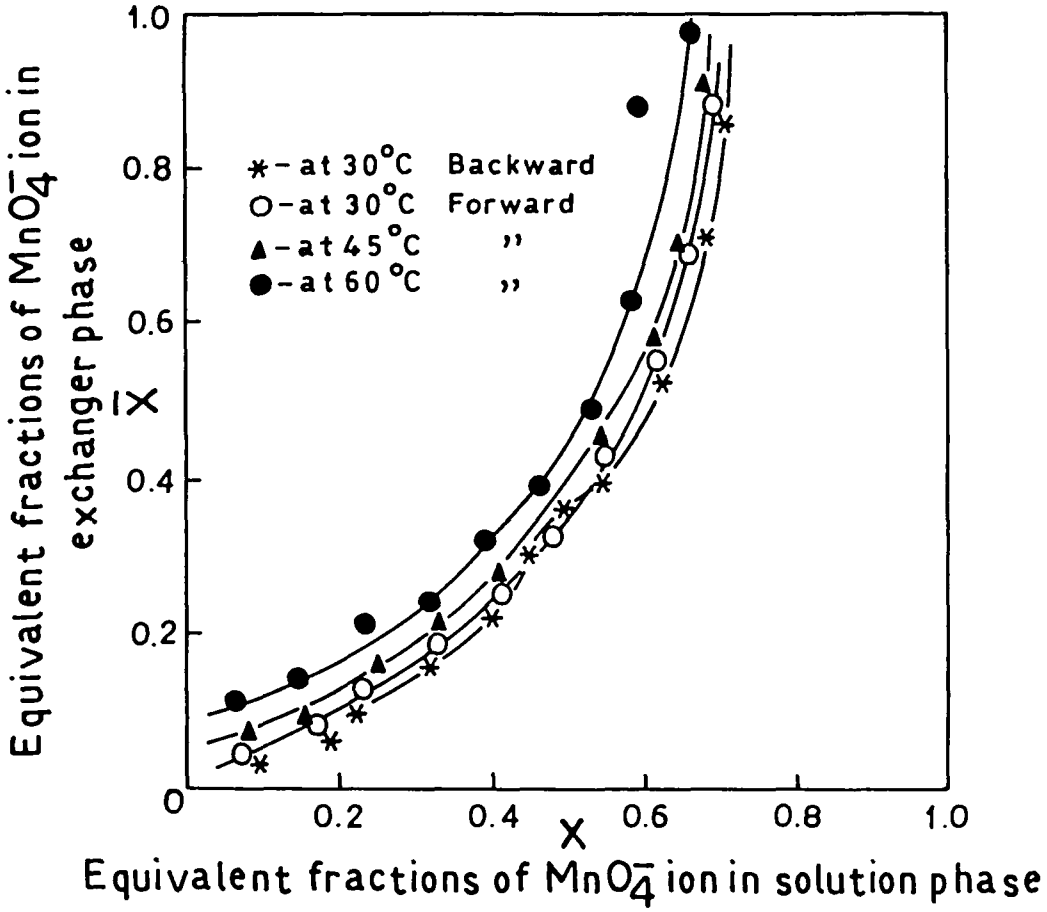


Fig: 9-Ion exchange isotherm of MnO_4^- ion on thoriumtetracyclohexylamine.

Table 14 (Continued)

X MnO_4^-	$\bar{X}$ MnO_4^-	Kc	Ka
	MnO_4^- - NO_3^- at 60 ± 1°C		
0.6550	0.9718	0.5226	
0.5900	0.8732	0.6949	
0.5750	0.6338	0.7391	
0.5250	0.4929	0.9048	
0.4610	0.3915	1.1690	0.034
0.3850	0.3239	1.5970	
0.3150	0.2394	2.1750	
0.2250	0.2113	3.4440	
0.1500	0.1408	5.6670	
0.0600	0.1127	15.6700	

Table 15

Equivalent fractions of CrO_4^{-2}, selectivity coefficients and thermodyanic equilibrium constants for CrO_4^{-2} - NO_3^- exchange on thoriumtetracylohexylamine

X CrO_4^{-2}	$\bar{X}$ CrO_4^{-2}	Kc	Ka
	CrO_4^{-2}- NO_3^- at 30 ± 1°C		
0.2109	0.7965	1.8473	
0.1729	0.7211	2.3619	
0.1043	0.7133	4.2400	
0.0662	0.6804	6.9646	
0.0463	0.6030	10.1777	33.40
0.0307	0.5194	15.570	
0.0235	0.4156	20.557	
0.0168	0.3117	28.820	
0.0107	0.2078	28.131	
5.15×10^{-3}	0.1039	95.365	
	CrO_4^{-2}- NO_3^- at 45 ± 1°C		
0.2000	0.8148	1.9677	
0.1664	0.7433	2.7277	
0.0997	0.7333	4.5846	
0.0613	0.6926	7.5631	
0.0433	0.6111	10.9220	42.35
0.0272	0.5296	17.6394	
0.0194	0.4278	24.7895	
0.0214	0.3259	39.3157	
5.92×10^{-3}	0.2241	82.6780	
2.86×10^{-3}	0.1120	172.450	

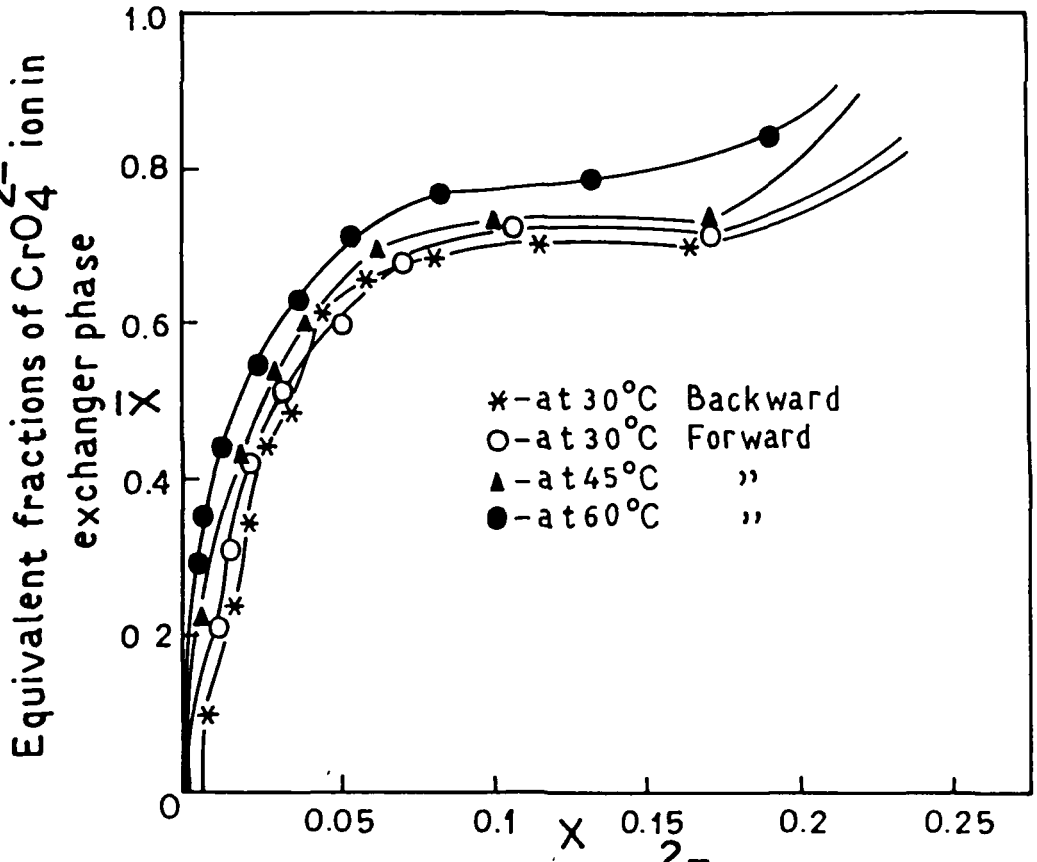


Fig:10-Ion exchange isotherm of CrO_4^{2-} ion on thoriumtetracyclohexylamine.

Table 15 (Continued)

X CrO_4^{-2}	$\bar{X}$ CrO_4^{-2}	Kc	Ka
	CrO_4^{-2}- NO_3^- at 60 ± 1°C		
0.1881	0.8352	2.1310	
0.1349	0.7944	3.1659	
0.0817	0.7740	4.5644	
0.0532	0.7130	8.7846	
0.0388	0.6233	12.2450	56.80
0.0258	0.5337	18.6200	
0.0168	0.4359	28.844	
6.16×10^{-3}	0.3463	79.6260	
3.55×10^{-3}	0.2322	138.4600	
2.85×10^{-3}	0.1120	172.4500	

The plots of lnKc Vs equivalent fractions of anions in exchanger phase are presented in figures11-14. The thermodynamic equilibrium constants are calculated from these plots and are given in table 16.

The values of enthalpy change ΔH^o, free energy change ΔG^o and entropy change ΔS^o were calculated. The results of these thermodynamic parameters are given in table 16.

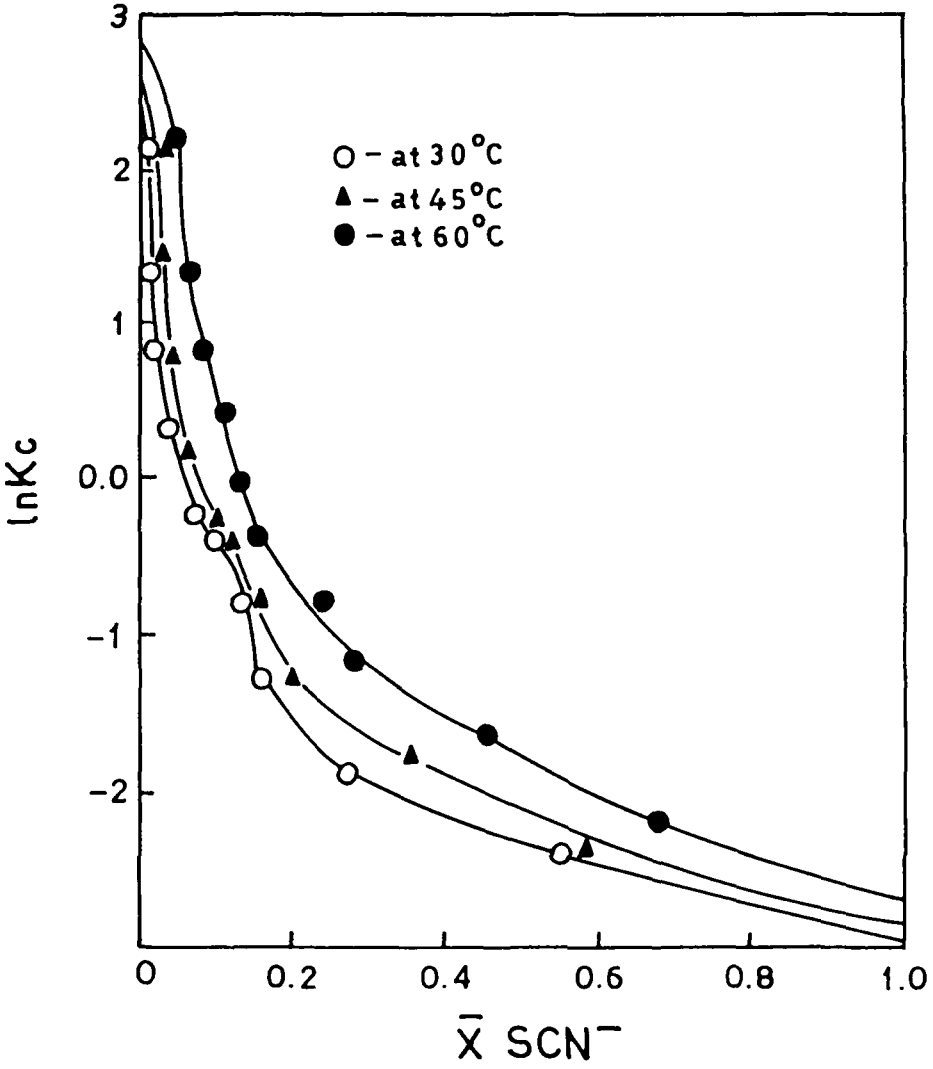


Fig:11-Selectivity coefficients vs equivalent fractions of SCN^- ion in exchanger phase.

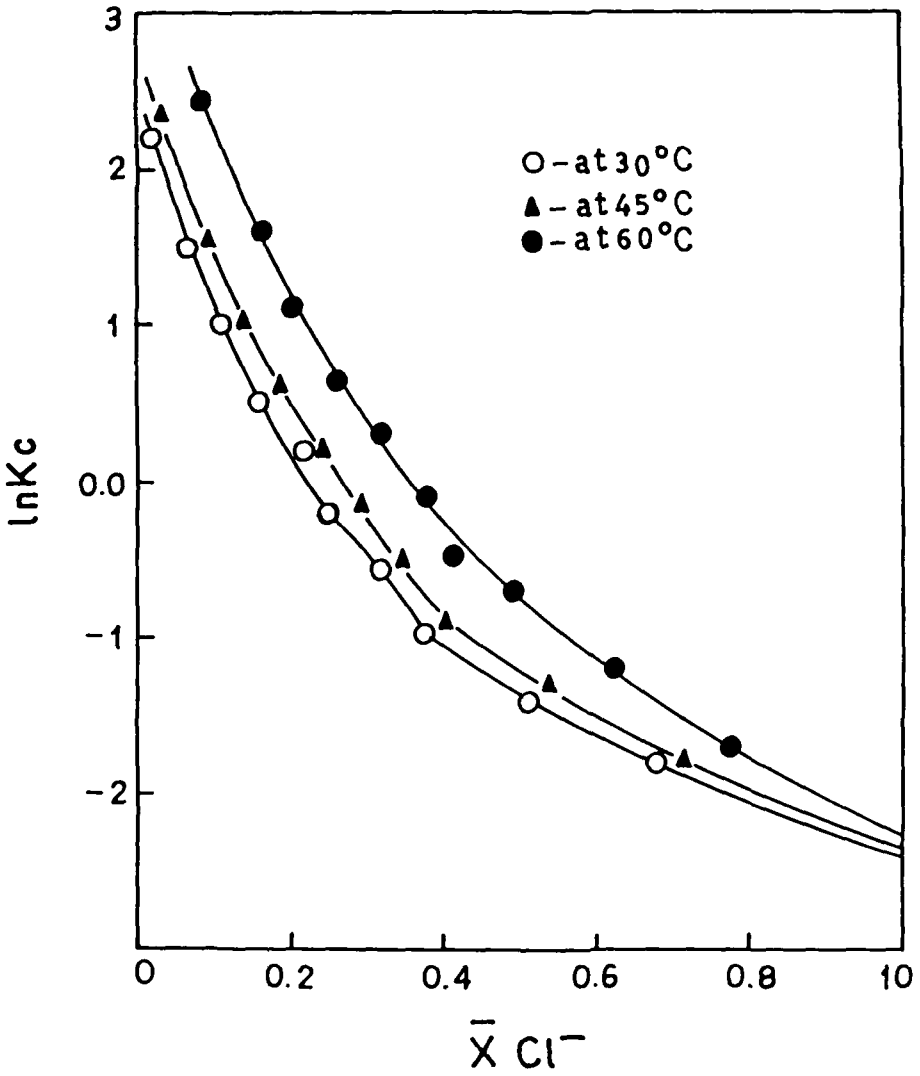


Fig:12-Selectivity coefficients vs equivalent fractions of Cl^- ion in exchanger phase.

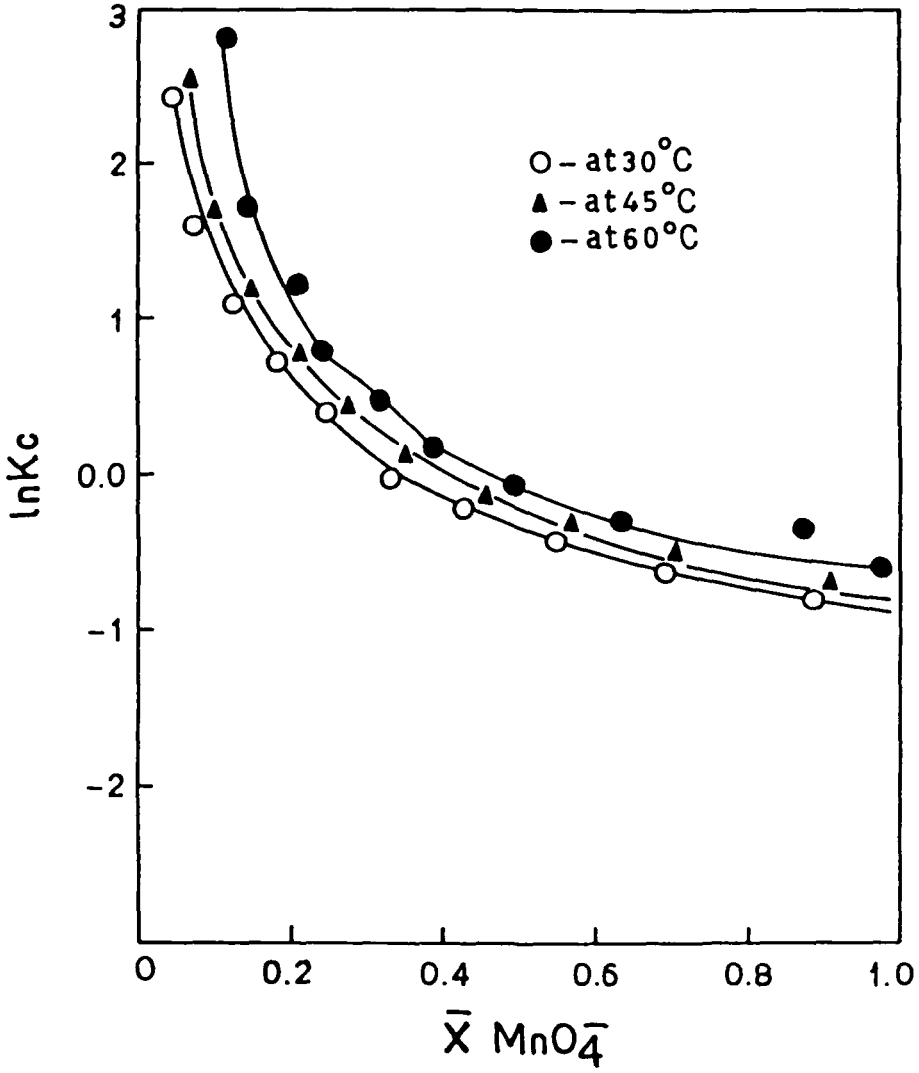


Fig:13 - Selectivity coefficients vs equivalent fractions of MnO_4^- ion in exchanger phase.

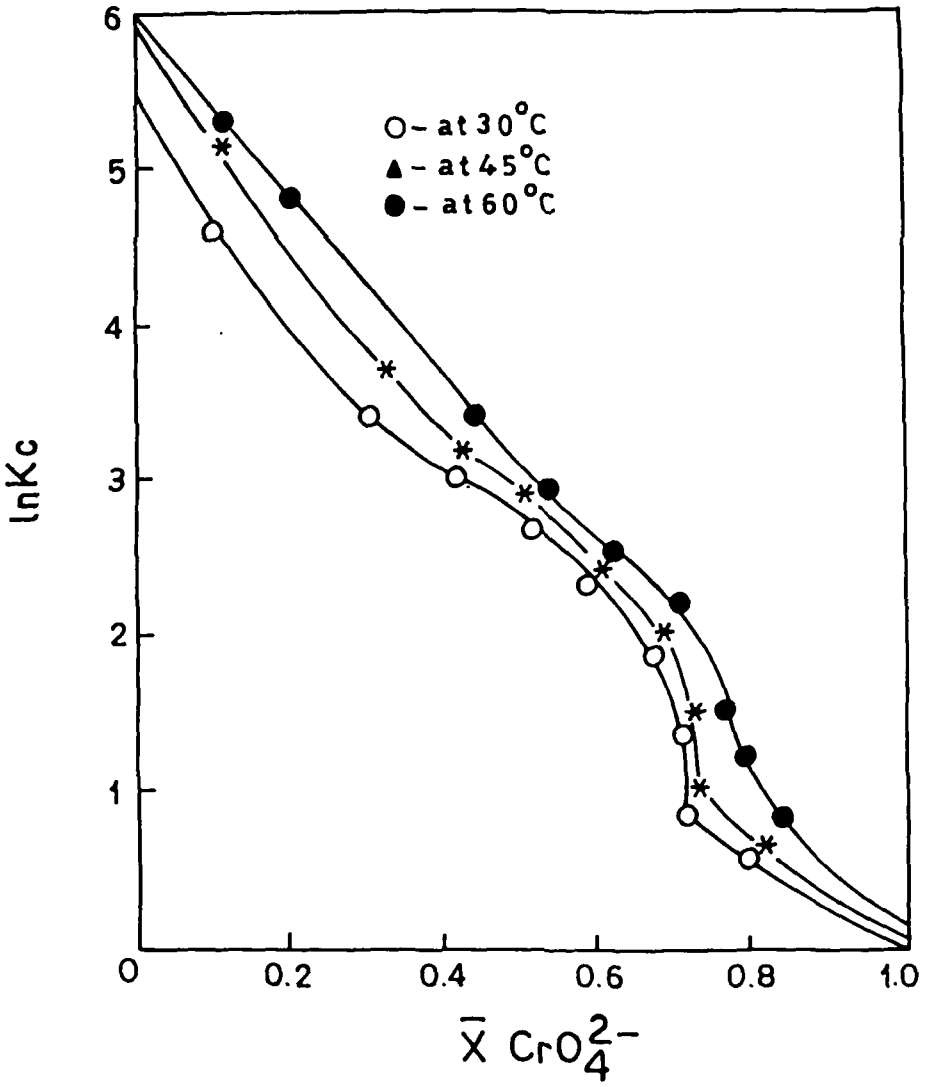


Fig:14-Selectivity coeffients vs equivalent fractions of CrO_4^{2-} ion in exchanger phase.

Table 16

Thermodynamic parameters on thoriumtetracyclohexylamine at constant ionic strength

S.No.	Anions	Ka			$\Delta G^{o}K$ J mol^{-1}			ΔH^{o} KJ Mol^{-1}	ΔS^{o} $J.mol^{-1}deg^{-1}$
		30°C	45°C	60°C	30°C	45°C	60°C	30 - 60°C	
1.	CrO_4^{2-}	33.40	42.350	56.800	-8.34	-9.90	-11.18	12.69	71.28
2.	MnO_4^{-}	0.052	0.047	0.034	7.47	8.39	9.37	-11.34	-62.49
3.	SCN^{-}	0.355	0.267	0.210	2.61	3.49	4.38	-14.67	-54.71
4.	Cl^{-}	0.140	0.110	0.073	4.99	5.96	7.26	-17.91	-75.40

DISCUSSION

The conditions of synthesis of thoriumtetracyclohexylamine (table 5) show that complete precipitation of the product occured when the metal-amine ratio was maintained at 1:4. The yield of the precipitate was also maximum at this ratio. In rest of the samples, the yeild was low, precipitation was incomplete, the chemical stability was poor and the ion exchange capacity was also low. The product thoriumtetracyclohexylamine behaves as an anion exchanger. The anion exchange capacity is probably due to the development of a free positive charge on the nitrogen atom of the incorporated cyclohexylamine. The results of anion exchange capacity for various anions at different temperatures are given in table 6. The maximum ion-exchange capacity of inorganic ion exchangers have been known to vary extensively with the nature of anionic species, temperature, and concentration of anions in solution, while organic ion exchange resins have fairly constant ion exchange capacities due to their elastic structure. Our exchanger also shows the same behaviour, similar to other inorganic ion-exchangers. The sequence of ion exchange capacity of our exchanger for various anions is in the order of their hydrated ionic radii. The greater the hydrated radii, the lesser the ion exchange capacity. The cation exchange capacity in this case was nil, which shows that the exchanger thoriumtetracyclohexylamine contains no negative change on its matrix.

A strong tandency for metal sorption was however observed. This behaviour may possibly be due to the presence of lone pair of electrons on the nitrogen atom of the amino-group allowing its chelation with different metal ions. The results of sorption capacities are given in table 2. The variation in sorption capacities may be attributed to the incomplete complex formation. Table 7 shows the stability of thoriumtetracyclohexylamine in different solvents. The material can be utilized for the separation of anions involving neutral and dilute solutions of acids and bases. The results of the effect of temperature on capacity show that the capacity increases with the increase of temperature upto 60°C and then it remains constant upto 100°C and a sudden decrease in capacity was observed after further increase in temperature upto 300°C. This decrease in capacity after 120°C is probably due to the loss of amino group. The results are given in table 8 and plotted in figure 2.

The chemical as well as elemental analysis of the exchanger thoriumtetracyclohexylamine reveal that the thorium: cyclohexylamine ratio is approximately 1:4.

The results of p_H-titration plotted in figure 1 show that the exchanger behaves as a monofunctional anion exchanger. Hydrolysis studies show that the material hydrolyses appreciably, till forty minutes there was very small, gradual change in pH. After 50 minutes a sharp change in pH was observed after which

pH remains almost constant. The results are given in table 9.

Structural studies:

It is quite evident from the IR-spectrum plotted in figure 3 that the exchanger thoriumtetracyclohexylamine is in possession of amino group and the metal nitrogen bond. It confirms that in the formation of this exchanger, the amine is bonded with the metal forming the matrix. The structure of thoriumtetracyclohexylamine complex is highly complicated like some of the amine complexes with other metal ions. An indication of possible structure may be discussed in the light of IR-spectrum of the compound.

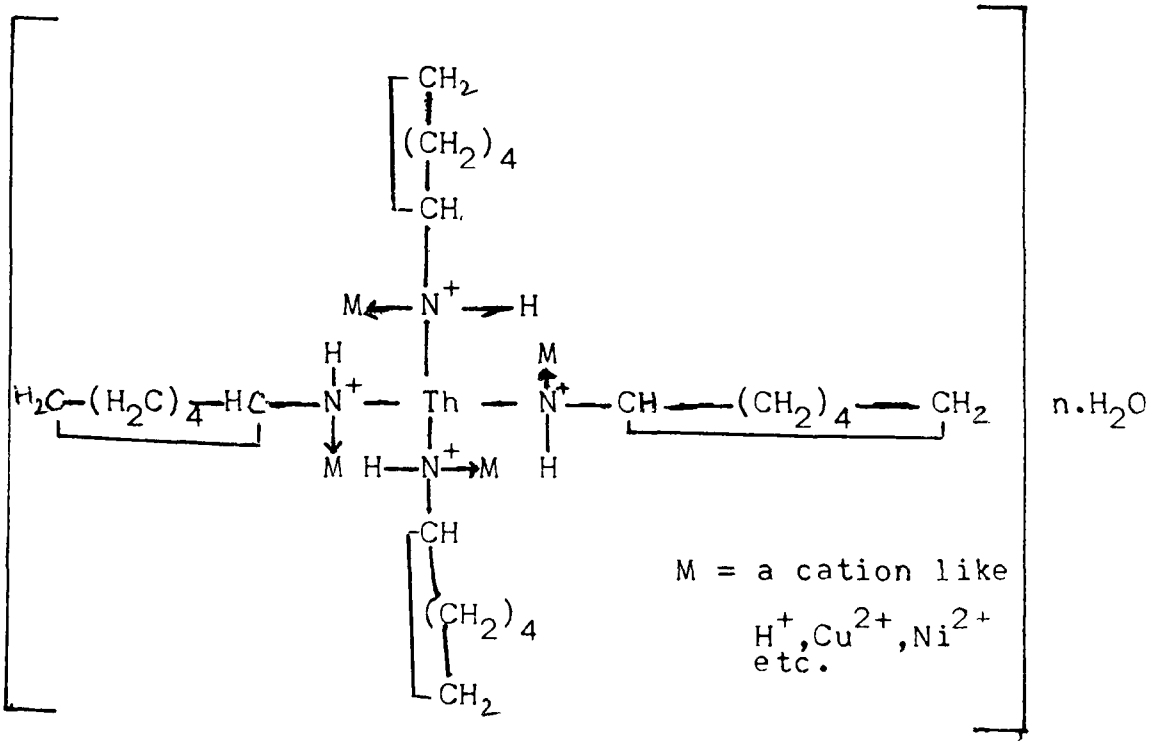
In the present study of thoriumtetracylohexylamine, the IR-spectrum shows a band between 3400-3100 cm^{-1} which is due to N-H stretching vibration, another band between 1550-1450 cm^{-1} is due to C-H stretching vibration. A minor peak is also seen at 1020 cm^{-1} which is due to C-N stretching vibration. Further a diffused band at 500 cm^{-1} show the M-N stretching vibration.

In the region 3500-2500 cm^{-1} there are three peaks in a neat sample of cyclohexylamine (figure 3a) i.e. at 3250 cm^{-1} (N-H), 2930 cm^{-1} (-CH) and 2860 cm^{-1} ($-CH_2$ scissoring). However when cyclohexylamine is complexed with thorium salt to give the exchanger complex, a very broad band appears in this region which perhaps masks the individual absorptions, such situations are expected in the IR-spectra of amine salts. The IR-spectra of

amine salts in solid state are often slighly different than those in solution phase.

The IR-spectra of neat sample of cyclohexylamine (figure 3a) also showed two peaks at 850 cm^{-1} and 1375 cm^{-1}. The NO_3^- absorptions also fall exactly at the same frequencies when the exchanger is taken in NO_3^- form, while the exchanger in Cl^- form (figure 3a) shows only broad bands at these frequencies. This shows that probably all the NO_3^- has been exchanged for Cl^- and the broad bands are due to cyclohexylamine absorptions in this region.

Thus, on the basis of IR, chemical composition and element analysis, the following structure may be postulated.



The distribution coefficient values given in table 10 show that Kd values of anions are quite high in the absence of

sodium hydroxide and these values decrease with the increase in concentration of sodium hydroxide. This behaviour shows that exchanger thoriumtetracyclohexylamine has high affinity for hydroxide ions as compared to other anions studied.

Owing to large differences in the distribution coefficient values of various anions, various analytically important separations were tried. Separation of CrO_4^{2-} from Br^-, I^- and SCN^- and $Cr_2O_7^{2-}$ from Br^-, I^- and SCN^- were successfully achieved (Table 11). These results also show high selectivity towards CrO_4^{2-} and $Cr_2O_7^{2-}$ ions as predicted from table 11.

The values of exchange for $SCN^- - NO_3^-$, $Cl^- - NO_3^-$, $MnO_4^- - NO_3^-$ and $CrO_4^{2-} - NO_3^-$ at different temperatures showing the reversibility of exchange of anions with nitrate form of exchanger are given in figures 7-10.

The ion exchange reaction for monovalent ions may be written as

$$\bar{N}O_3^- + A^- \rightleftharpoons \bar{A}^- + NO_3^- \qquad \ldots\ (i)$$

and for bivalent ions,

$$2\bar{N}O_3^- + A^{2-} \rightleftharpoons \bar{A}^{2-} + 2NO_3^- \qquad \ldots\ (ii)$$

The barred quantities refer to the exchanger phase and unbarred to aqueous phase.

The selectivity coefficients are calculated from the relationship given by R.M. Barrer and R.P. Townsend[10], for monovalent exchange

$$Kc = \frac{\bar{X}A^{-}.\ XNO_3^{-}}{\bar{X}NO_3^{-}.\ XA^{-}} \quad \frac{\gamma NO_3^{-}}{\gamma A^{-}} \qquad \ldots\ (iii)$$

and for bivalent exchange

$$Kc = \frac{\bar{X}A^{2-}.\ X^2NO_3^{-}}{\bar{X}^2NO_3^{-}.\ XA^{2-}} \quad \frac{\gamma^2NO_3^{-}}{\gamma A^{2-}} \qquad \ldots\ (iv)$$

where XA is the equivalent fraction of anion in the exchanger phase, $\bar{X}NO_3^{-}$, the equivalent fraction of nitrate in exchanger phase, XNO_3^{-} and XA^{-} are the equivalent fractions of nitrate and the competing anion in the aqueous phase respectively. Where as γNO_3^{-} and γA^{-} are the activity coefficients of nitrate and the competing anion in the equeous phase. The activity of anions in aqueous phase is calculated using Debye-Huckel equation

$$-\log fi = \frac{A.Zi^2\sqrt{\mu}}{1+B.\ ai\sqrt{\mu}} \qquad \ldots\ (v)$$

where A and B are the constants, ai, the ion size parameter, μ, the ionic strength and Zi is the charge of the ion i. The selectivity coefficient values are plotted in figures 11-14. These results show that the values of selectivity coefficient (Kc) does not remain constant but varies with the increasing concentration of anion (A) in solution, hence Ka can be evaluated. Ka the thermodynamic equilibrium constant is calculated from the expression given by Gaines and Thomas

$$\ln Ka = (ZA^{-} - ZNO_3^{-}) + \int_0^1 \ln Kc \ d\ \bar{X}_A - \ldots\ (vi)$$

The values of Ka, are calculated from the plots of lnKa Vs $\bar{X}_{A^-}$. The standard free energy (ΔG^o) is calculated from thermodynamic equilirbium constant using the equation

$$\Delta G^o = \frac{RT}{ZNO_3^- \cdot ZA^-} \ln Ka \qquad \ldots\ldots (vii)$$

where R is the gas constant, ZNO_3^- and ZA^- are the valencies of nitrate and the competing anion and T is the absolute temperature.

The values of ΔG^o are given in table 16. The free energy change is positive in all cases except for CrO_4^{2-}. This shows that for monovalent anion the exchange process is non-spontaneous.

The values of changes in thermodynamic quantities ΔH^o and ΔS^o are calculated from the respective equilibrium constants are follows

$$\Delta H^o = - R \frac{d (\ln Ka)}{d (1/T)} \qquad \ldots\ldots (viii)$$

and $$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \qquad \ldots\ldots (ix)$$

The standard enthalpy changes ΔH^o and entropy changes ΔS^o are presented in table 16. The entropy loss in case of SCN^-, MnO_4^- and Cl^- is an indication of greater order produced in the forward reaction, when SCN^-, Cl^- and MnO_4^- were transfered to thoriumtetracyclohexylamine. It reflects that the solvation entropy of NO_3^- is greater than the competing anion. Whereas

the enthalpy loss in case of SCN^-, Cl^- and MnO_4^- is an indication of exothermic reaction. This shows that the binding energy of competing anion is less than that of nitrate ion.

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C H A P T E R - III

MECHANISM OF ANION EXCHANGE ON THORIUMTETRACYCLOHEXYLAMINE

The applications of inorganic ion exchangers are increasing at an exponential rate dueto their resistance to heat and radiations. Now the applications of these ion-exchangers are also being utilized in the fields of heterogeneous catalysis, solid electrolytes, inorganic ion exchange membranes and ion selective electrodes. In most of these fields, informations about the ion exchange kinetics and the mobility of counter ions are required.

Kinetics play an important role in the study of the mechanism of ion exchange. Kinetic studies on ion exchangers were mainly started by Nachod and Wood[1]. Nancollas and Paterson[2] described the quantitative measurements on hydrous thoria and Zirconia. Some studies on kinetics of ion exchange on inorganic ion exchangers have been reported[3-12]. In order to understand the mechanism of ion exchange on the granules of thoriumtetracyclohexylamine, studies are summerized in this chapter. Experimental approaches have been used to show the rate of diffusion through particle. Energies of activation and other parameters are calculated.

EXPERIMENTAL

Reagents:

Thorium nitrate (Fissions USA) and cyclohexylamine (BDH, England) were used. All other chemicals used were of analytical reagent grade.

Synthesis:

The ion exchanger throiumtetracyclohexylamine[13] was synthesized by mixing 0.10 M solutions of thorium nitrate and cyclohexylamine in the volume ratio of 1:4. The precipitate obtained was kept standing for 24 h, after which it was filtered and washed with deionized water and dried at 40°C in an air oven. It was broken in small particles simply by immersing in de-ionized water. The exchanger granules were then converted to nitrate form by treating with 0.10 M solution of potassium nitrate for 24 h with occasional shaking. Finally it was washed several times and dried at 40°C.

Kinetic measurements:

Rates of exchange were measured by limited bath technique. The exchanger was finely ground and sized by standard sieves to get particles of different mesh sizes (50-100, 100-150, 150-200 and 200-300), particles of mean radius 1.12×10^{-3} cm (mesh size 50-100) were used for studies unless otherwise stated. Solutions of anions (0.10 N) at constant ionic strength were thermostated at the required temperature in stoppered conical flasks. A weighed amount of the exchanger (0.500 g) was added and the flasks were thoroughly shaken. After appropriate intervals the contents of the flasks were filtered using whatman No. 42 filter paper and titrated. The ion diffusion studies were conducted at 40, 50 and 60 ± 1°C.

Interruption test:

In order to carry out the interruption test, the above procedure was applied for another set and after specified time (15 and 20 minutes) the exchanger particles were removed from the adhering solution. After 10 minutes break they were reimmersed in their respective flasks and the experiment continued. The CrO_4^{2-} content in the supernatant was then determined at various time intervals.

RESULTS

The interruption test was performed for CrO_4^{2-} - NO_3^- exchange on thoriumtetracyclohexylamine in nitrate form. The F values as a function of time before and after interruption of 10 minutes at 40°C are given in table 17 and 17a and are plotted in figure 15.

Table 17

Interruption test for CrO_4^{2-} - NO_3^- exchange on thoriumtetracyclohexylamine at 40 ± 1°C.

Interruption applied after 15 minutes of shaking

S.No.	Time (minutes)	F
1.	2	0.318
2.	5	0.480
3.	10	0.615
4.	15	0.722
5.	10 minutes	Interruption
	0	0.742
6.	5	0.810
7.	10	0.852
8.	15	0.896
9.	20	0.921

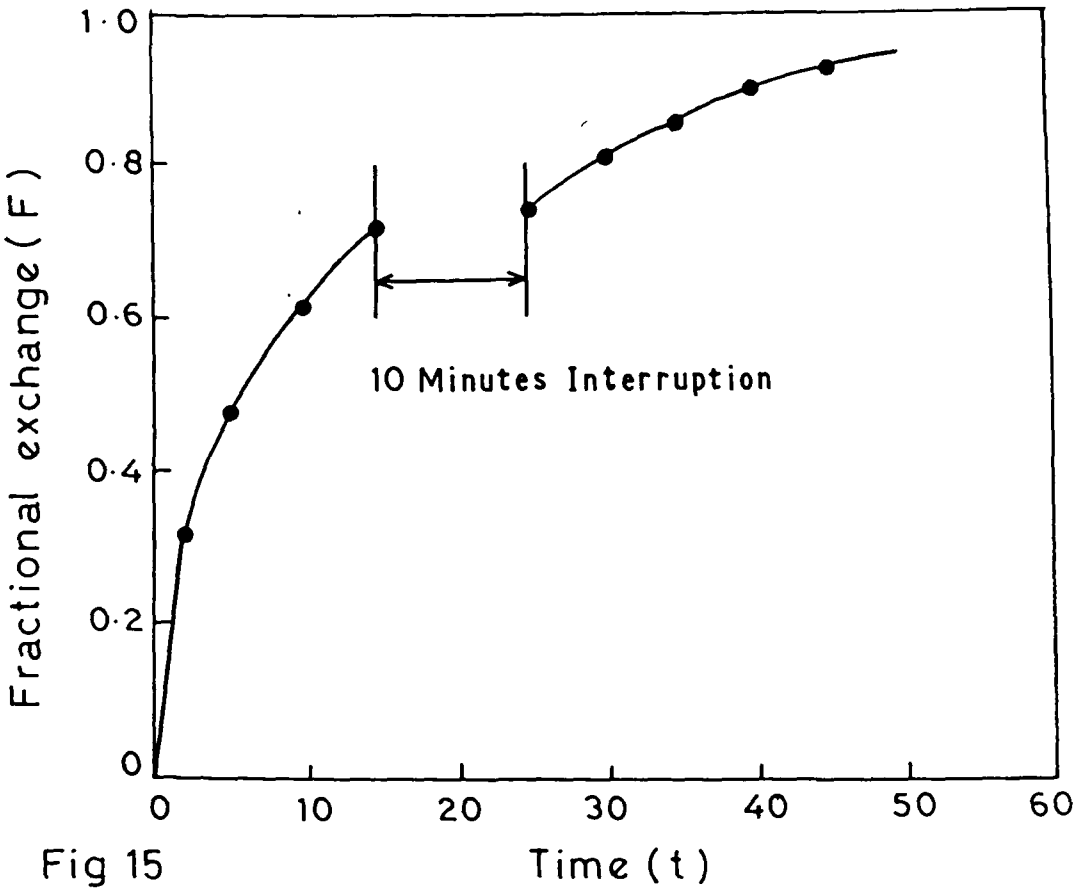

Fig 15

Effect of an interruption on the rate of CrO_4^{2-}—NO_3^- exchange on thoriumtetracyclohexylamine

17 a Interruption applied after 20 minutes of shaking

S.No.	Time (minutes)	F
1.	2	0.316
2.	5	0.475
3.	10	0.316
4.	15	0.724
5.	20	0.799
	10 minutes	Interruption
6.	0	0.823
7.	5	0.861
8.	10	0.892
9.	15	0.932
10.	20	0.951
11.	25	0.984

Effect of temperature:

In order to see the effect of temperature, the kinetics was performed for CrO_4^{2-}, MnO_4^-, Cl^- and SCN^- ions at three different temperatures viz. 40, 50 and 60 $\pm$ 1°C. F values as a function of time are calculated and the corresponding Bt values are taken as tabulated by Reichenberg[14], the results given in table 18-20 and the results of F VS time at different temperature for the above mentioned anions are plotted in figures 16-18 while the results of Bt VS t are plotted in figures 19-22.

Table 18

F and Bt values as function of time for different anions on thoriumtetracyclohexylamine at 40 ± 1°C

t, min.	F.	Bt.	t, min.	F.	Bt.
		CrO_4^{2-} - NO_3^- exchange			
2	0.3150	0.1031	45	0.9500	2.5000
5	0.4800	0.2730	50	0.9630	2.7701
10	0.6340	0.5541	55	0.9720	3.0770
15	0.7330	0.8413	60	0.9780	3.3190
20	0.8050	1.1420	65	0.9830	3.5773
25	0.8500	1.4040	70	0.9870	3.8451
30	0.8840	1.6604	75	1.0000	-
35	0.9120	1.9330	80	1.0000	-
40	0.9340	2.2201	--	-	-
		MnO_4^- - NO_3^- exchange			
2	0.2950	0.0892	45	0.9240	2.0793
5	0.4410	0.2220	50	0.9400	2.3200
10	0.5830	0.4430	55	0.9543	2.5184
15	0.6770	0.6650	60	0.9630	2.7991
20	0.7500	0.9050	65	0.9711	3.0427
25	0.8100	1.1710	70	0.9770	3.2745
30	0.8450	1.3698	75	1.0000	-
35	0.8800	1.6230	80	1.0000	-
40	0.9051	1.8560	--	-	-

t, min.	F.	Bt.	t, min.	F.	Bt.
		$Cl^- - NO_3^-$ exchange			
2	0.2800	0.0767	45	0.9060	1.8800
5	0.4030	0.1800	50	0.9230	2.0662
10	0.5580	0.3960	55	0.9390	2.3000
15	0.6520	0.5980	60	0.9510	2.5180
20	0.7250	0.8130	65	0.9600	2.7240
25	0.7820	1.0355	70	0.9670	2.9140
30	0.8200	1.2240	75	0.9740	3.1500
35	0.8560	1.4400	80	1.0000	-
40	0.8850	1.6700	--	-	-
		$SCN^- - NO_3^-$ exchange			
2	0.2610	0.0688	45	0.8830	1.6010
5	0.3900	0.1670	50	0.8990	1.7940
10	0.5200	0.3320	55	0.9160	1.9790
15	0.6200	0.5220	60	0.9280	2.1633
20	0.6900	0.6990	65	0.9440	2.3200
25	0.7410	0.8715	70	0.9501	2.5100
30	0.7900	1.0730	75	0.9570	2.6490
35	0.8250	1.2440	80	1.0000	-
40	0.8550	1.4330	--	-	-

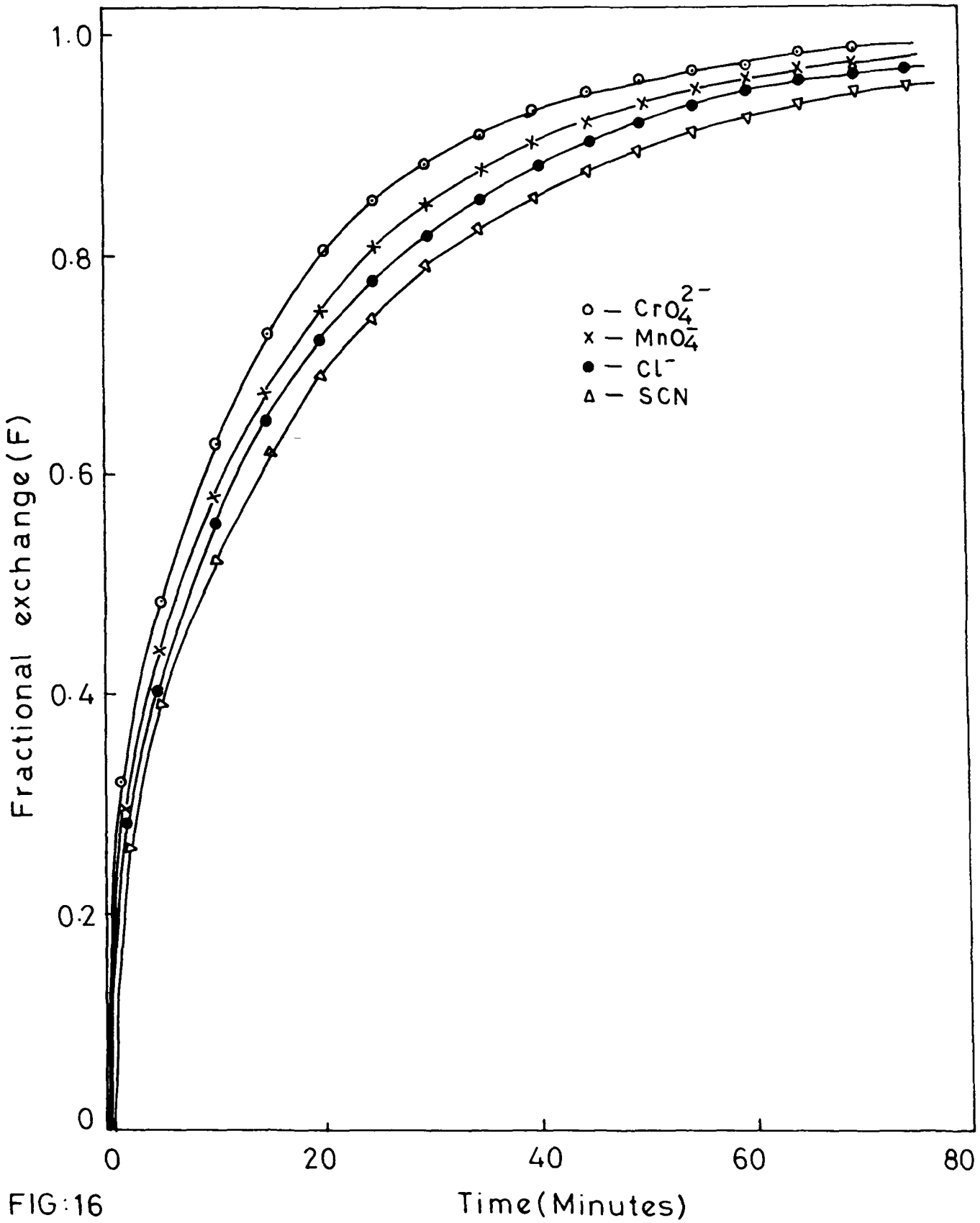

FIG:16

Rate of exchange of different anions at 40 °C on thoriumtetracyclohexylamine.

Table 19

F and Bt values as function of time for different anions on thoriumtetracyclohexylamine at 50 ± 1°C.

t, min.	F.	Bt.	t, min.	F.	Bt.
		CrO_4^{2-} - NO_3^- exchange			
2	0.3400	0.1226	45	0.9540	2.6000
5	0.5020	0.3040	50	0.9660	2.8800
10	0.6570	0.6111	55	0.9760	3.2030
15	0.7460	0.8889	60	0.9810	3.4650
20	0.8140	1.1910	65	0.9860	3.7701
25	0.8600	1.4680	70	1.0000	-
30	0.8930	1.7372	75	-	-
35	0.9300	2.0300	80	-	-
40	0.9370	2.2670	--	-	-
		MnO_4^- - NO_3^- exchange			
2	0.3100	0.0988	45	0.9350	2.2350
5	0.4580	0.2440	50	0.9480	2.4590
10	0.6050	0.4886	55	0.9600	2.7200
15	0.7041	0.7453	60	0.9690	2.9760
20	0.7640	0.9590	65	0.9760	3.230
25	0.8200	1.2240	70	0.9810	3.4560
30	0.8620	1.4850	75	1.0000	-
35	0.8920	1.7270	80	-	-
40	0.9160	1.9790	--	-	-

t, min.	F.	Bt.	t, min.	F.	Bt.
		Cl^- - NO_3^- exchange			
2	0.2900	0.0861	45	0.9120	1.9330
5	0.4300	0.2100	50	0.9300	2.1600
10	0.5700	0.4190	55	0.9440	2.3850
15	0.6600	0.6280	60	0.9550	2.6010
20	0.7400	0.8680	65	0.9640	2.8300
25	0.7900	1.0700	70	0.9700	3.0100
30	0.8350	1.3079	75	0.700	3.2400
35	0.8640	1.5150	80	1.0000	-
40	0.8920	1.7300	--	-	-
		SCN^- - NO_3^- exchange			
2	0.2760	0.770	45	0.8900	1.7100
5	0.413	0.1908	50	0.9080	1.8900
10	0.5410	0.3660	55	0.9230	2.0700
15	0.6370	0.5610	60	0.9370	2.2670
20	0.7030	0.7420	65	0.9470	2.4400
25	0.7600	0.9440	70	0.9560	2.6300
30	0.8000	1.1200	75	0.9640	2.8300
35	0.8400	1.3400	80	1.0000	-
40	0.8670	1.5190	--	-	-

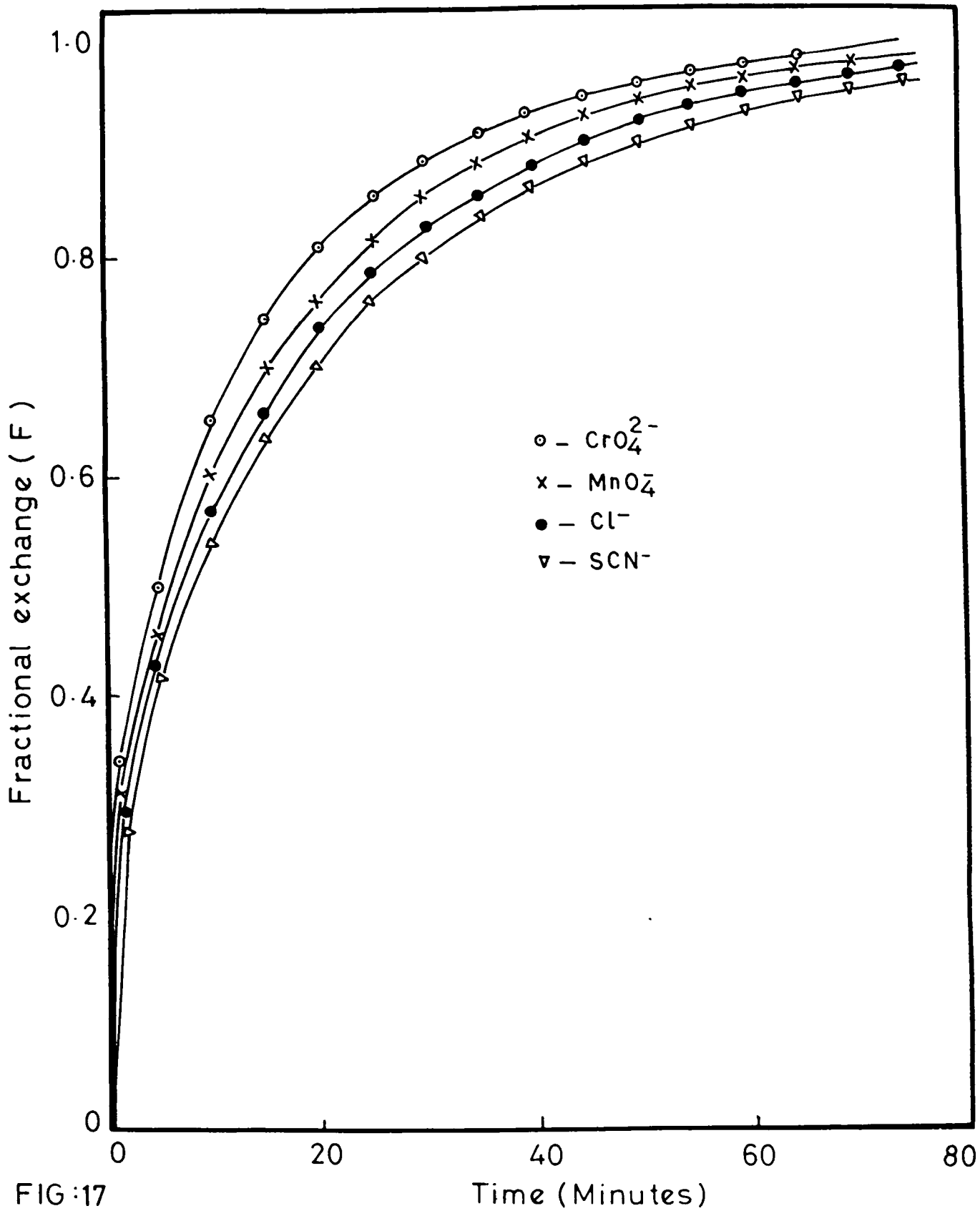

FIG:17

Rate of exchange of different anions at 50°C on thoriumtetracyclohexylamine

Table 20

F and Bt values as a function of time for different anion on thoriumtetracyclohexylamine at 60 ± 1°C.

t, min.	F.	Bt.	t, min.	F.	Bt.
		CrO_4^{2-} - NO_3^- exchange			
2	0.3530	0.1331	45	0.9620	2.7701
5	0.5180	0.3284	50	0.9720	3.0771
10	0.6740	0.6571	55	0.9790	3.3650
15	0.7640	0.9593	60	0.9850	3.7000
20	0.8260	1.2600	65	0.9890	4.0101
25	0.8720	1.5601	70	1.0000	-
30	0.9050	1.8606	75	-	-
35	0.9300	2.1610	80	-	-
40	0.9470	2.4550	--	-	-
		MnO_4^- - NO_3^- exchange			
2	0.3200	0.1080	45	0.9400	2.3200
5	0.4700	0.2590	50	0.9540	2.5814
10	0.6220	0.5220	55	0.9650	2.8564
15	0.7120	0.7708	60	0.9730	3.1142
20	0.7840	1.0477	65	0.9790	3.6550
25	0.8330	1.2961	70	0.9840	3.6015
30	0.8730	1.5580	75	1.0000	-
35	0.9000	1.8000	80	-	-
40	0.9230	2.0760	--	-	-

t, min.	F.	Bt.	t, min.	F.	Bt.
		$Cl^- - NO_3^-$ exchange			
2	0.2940	0.0885	45	0.9200	2.0300
5	0.4430	0.2250	50	0.9360	2.5100
10	0.5870	0.4510	55	0.9490	2.4780
15	0.6800	0.6750	60	0.9600	2.7200
20	0.7500	0.9050	65	0.9680	2.9443
25	0.8010	1.1400	70	0.9740	3.1519
30	0.8330	1.3500	75	0.9790	3.3655
35	0.8760	1.5890	80	1.0000	-
40	0.9010	1.8150	--	-	-
		$SCN^- - NO_3^-$ exchange			
2	0.3000	0.0928	45	0.8980	1.7851
5	0.4250	0.2040	50	0.9160	1.9790
10	0.5630	0.4050	55	0.9310	2.1759
15	0.6540	0.6040	60	0.9430	2.3669
20	0.7200	0.7980	65	0.9530	2.5590
25	0.7800	1.0280	70	0.9620	2.7700
30	0.8200	1.2340	75	0.9680	2.9440
35	0.8490	1.3950	80	1.0000	-
40	0.8760	1.5898	--	-	-

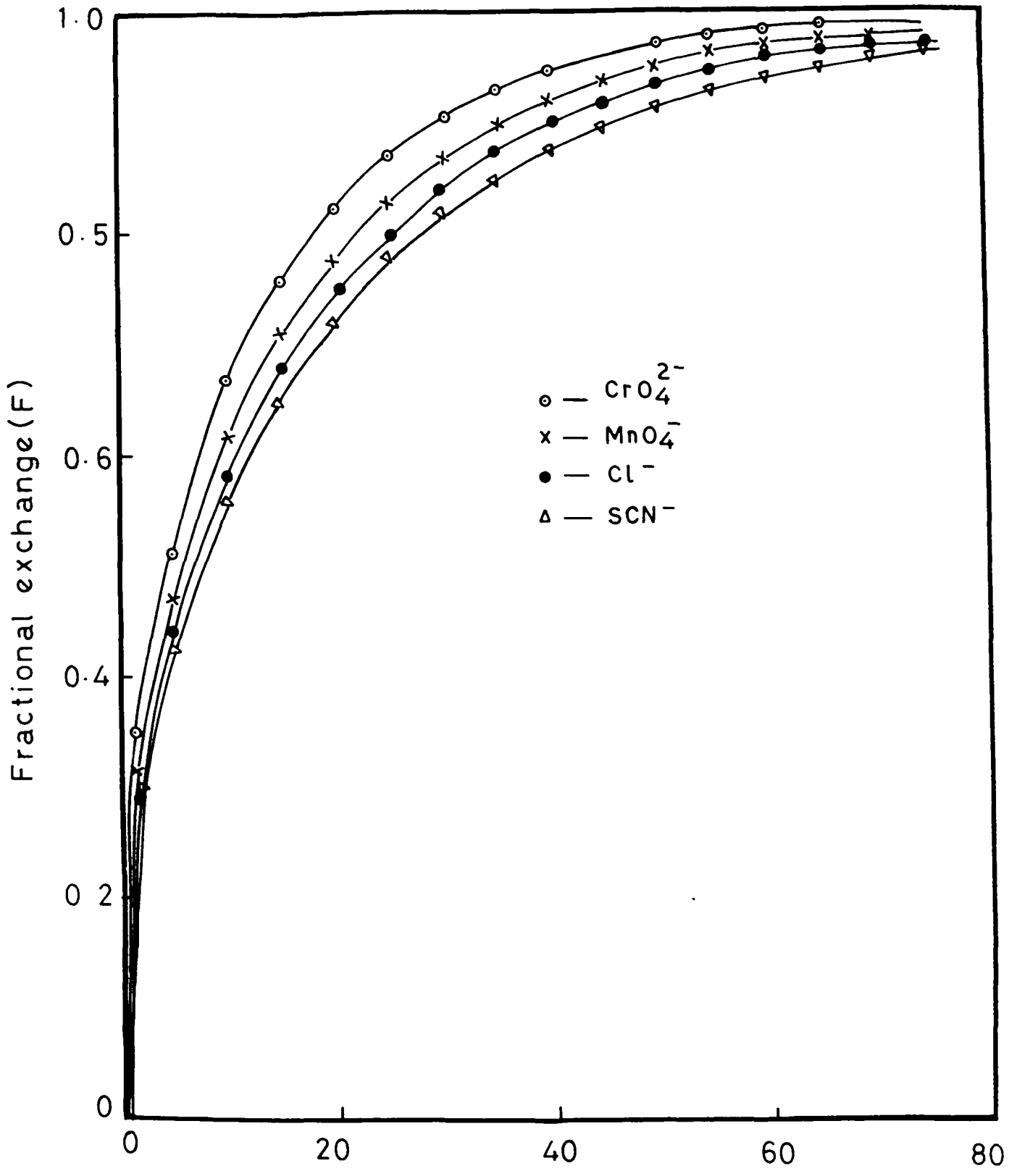

FIG:18

Rate of exchange of different anions at 60°C on thoriumtetracycloexylamine

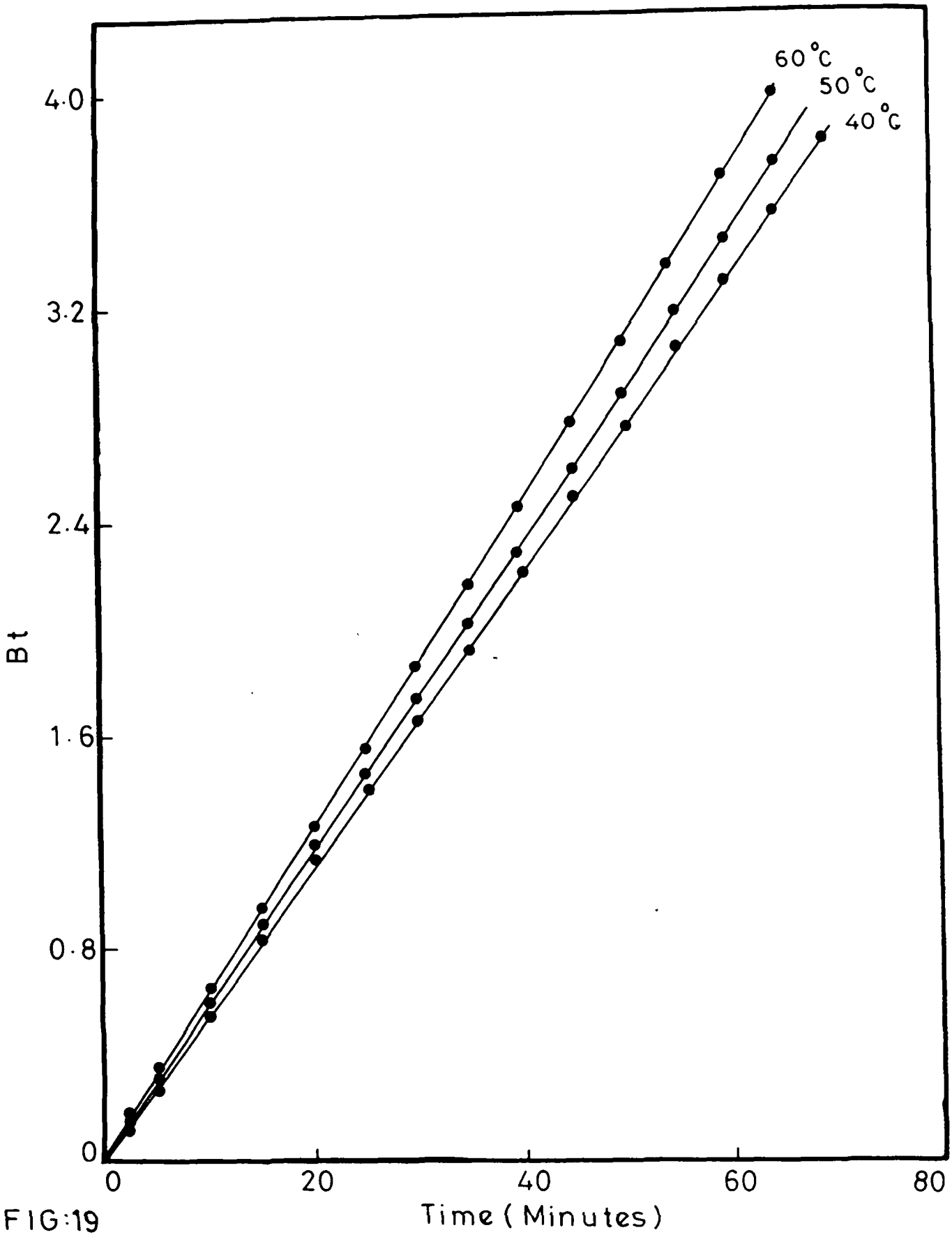

FIG:19

Effect of temperature on the rate of $CrO_4^{2-} - NO_3^-$ exchange on thorium tetracyclohexylamine

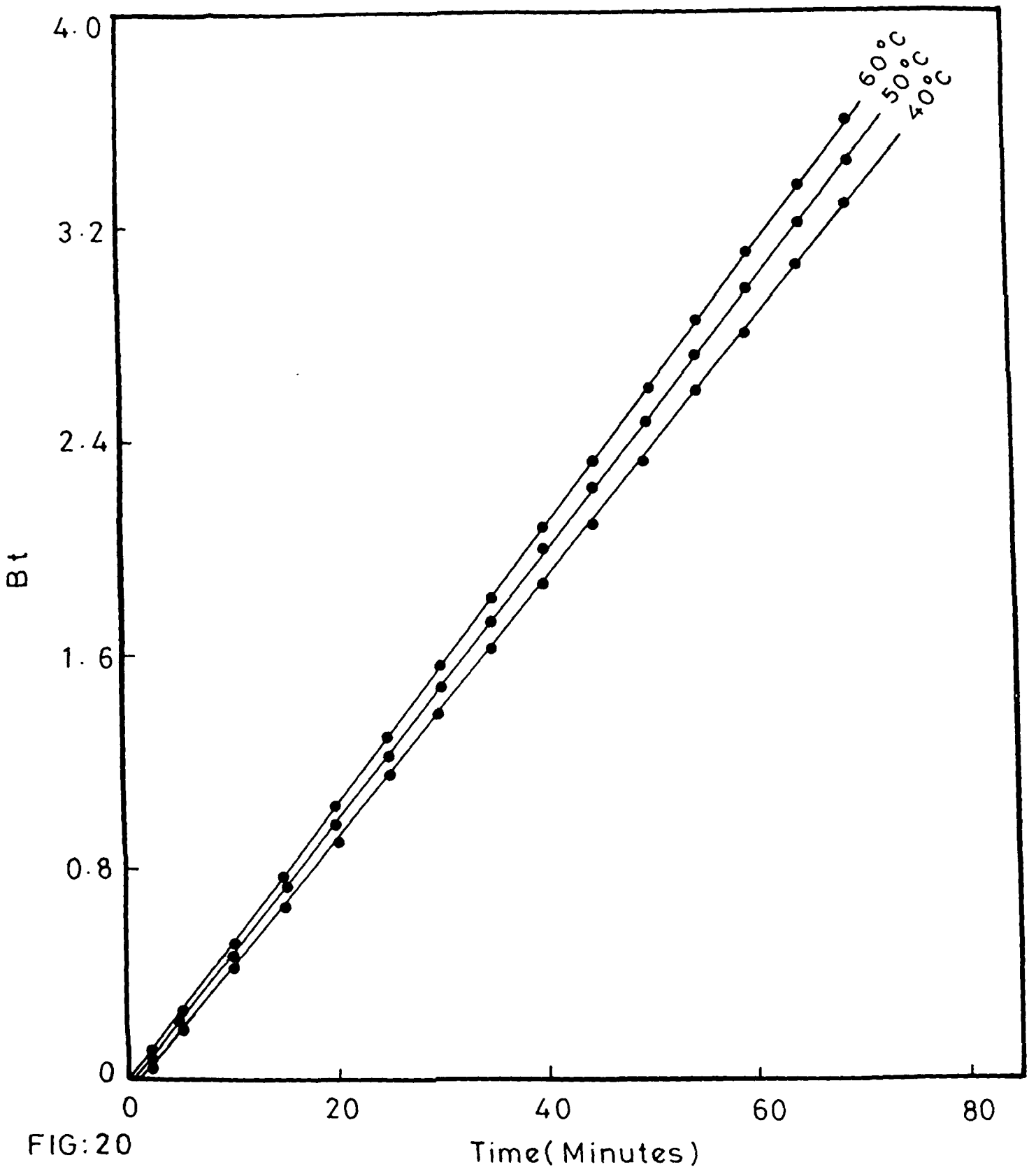

FIG: 20

Effect of temperature on the rate of MnO_4^- – NO_3^- exchange on thoriumtetracyclohexylamine

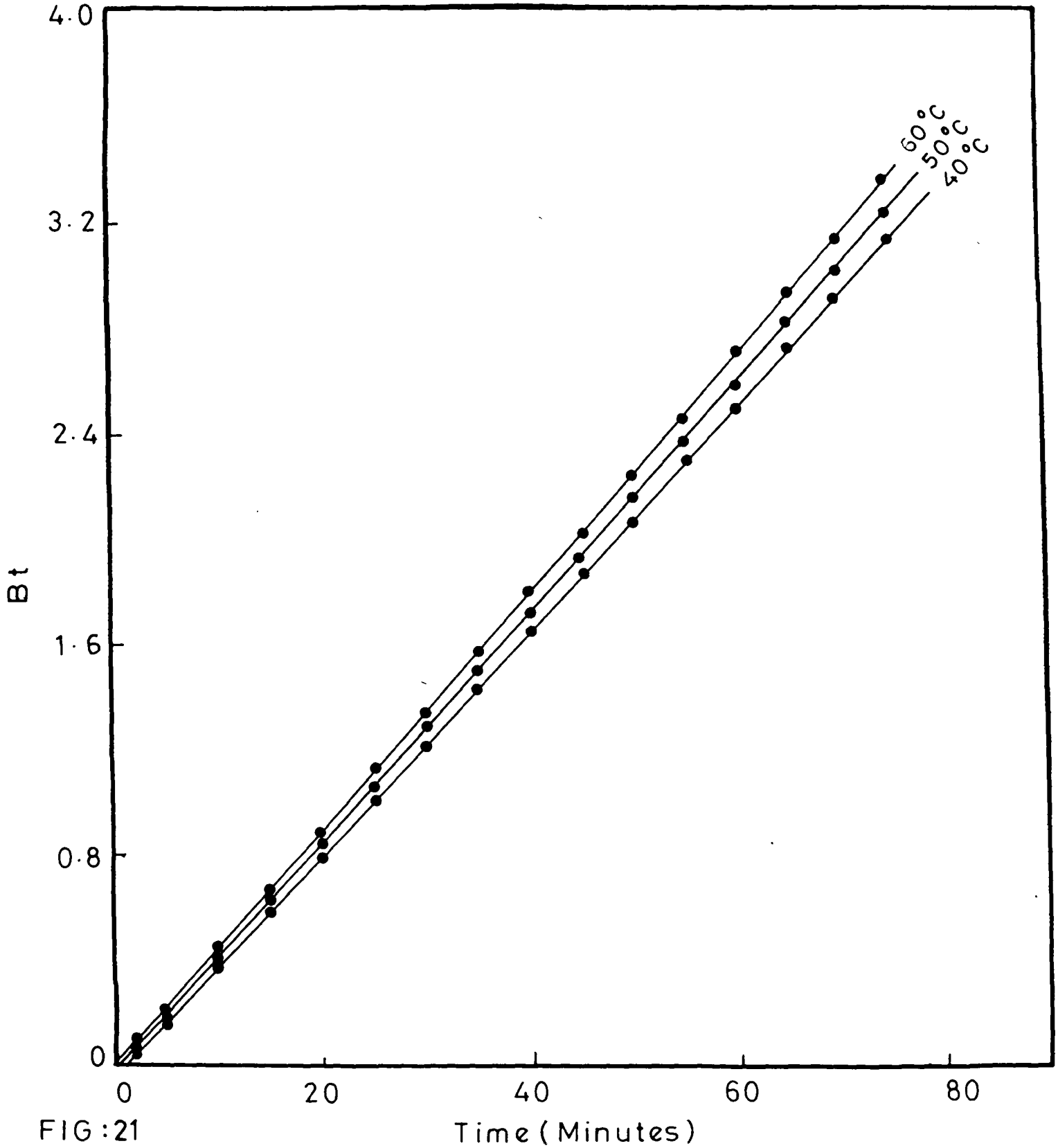

FIG:21

Effect of temperature on the rate of $Cl^- - NO_3^-$ exchange on thoriumtetracycloexylamine

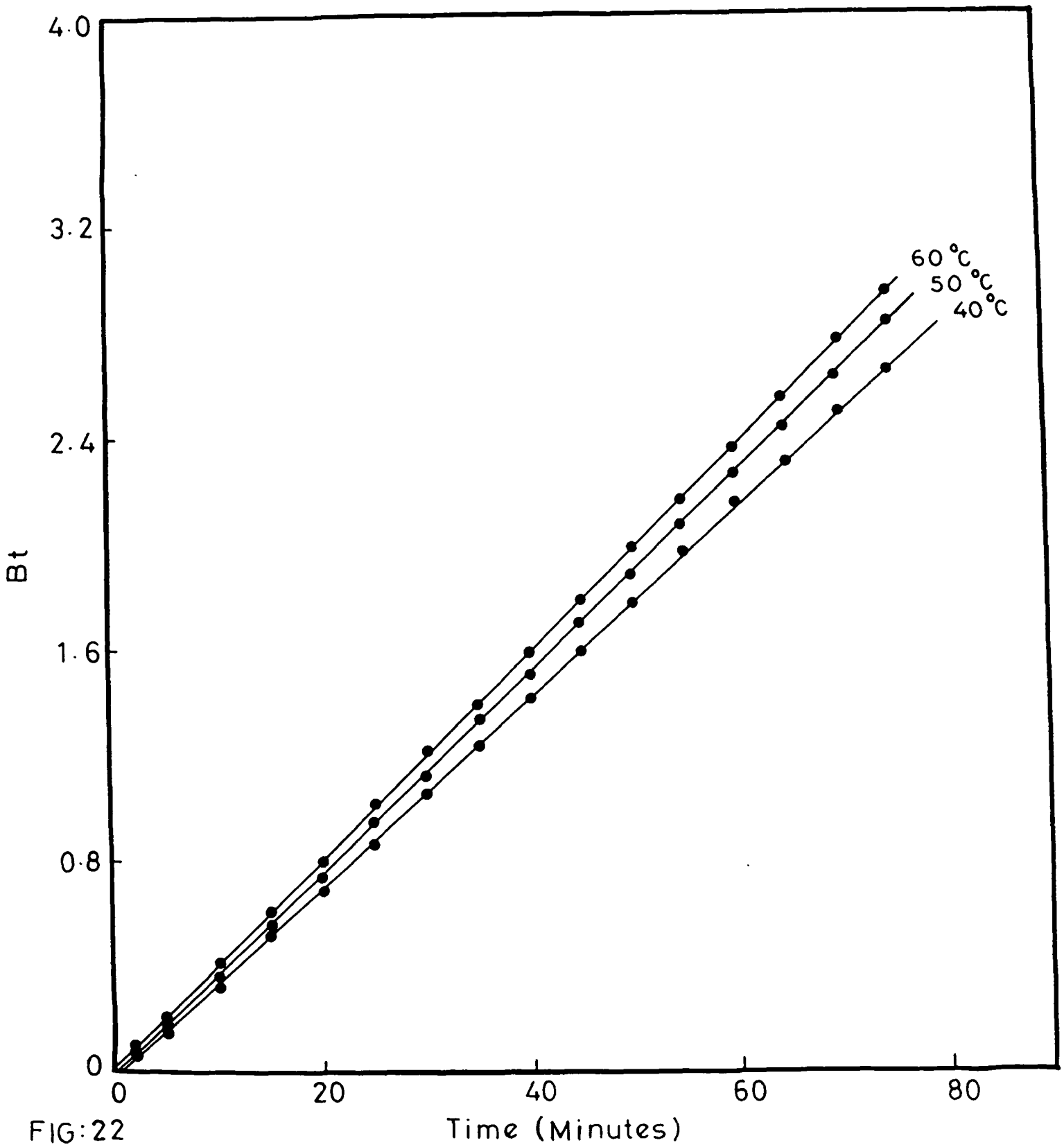

FIG:22

Effect of temperature on the rate of $SCN^{-}-NO_3^{-}$ exchange on thoriumtetracyclohexylamine

Effect of particle size:

The effect of particle size on the kinetics of ion exchange for three different particle sizes viz. 6.15×10^{-3}, 4.30×10^{-3} and 3.05×10^{-3} cm were performed. The results of F and Bt values as a function of particle size for $CrO_4^{2-} - NO_3^-$ exchange at 40°C are given in table 21. The F values as a function of time are plotted in figure 23 and the values of Bt Vs t are plotted in figure 24.

Table 21

F and Bt values as function of particle size for $CrO_4^{2-} - NO_3^-$ exchange on thoriumtetracyclohexylamine at 40±1°C.

t,min	F	Bt	t,tim	F	Bt
		For particle size 6.15×10^{-3} cm			
2	0.2800	0.0797	45	0.9560	2.5600
5	0.4810	0.2795	50	0.9670	2.8800
10	0.6380	0.5638	55	0.9740	3.1520
15	0.7340	0.8453	60	0.9810	3.4700
20	0.8000	1.1200	65	0.9850	3.7020
25	0.8500	1.4040	70	1.0000	-
30	0.8870	1.6827	75	-	-
35	0.9200	2.0300	80	-	-
40	0.9380	2.2830	--	-	-

Table 21 (Continued)

t,min	F	Bt	t,min	F	Bt
		For particle size 4.30×10^{-3} cm			
2	0.3204	0.1071	45	0.9630	2.7900
5	0.4860	0.2808	50	0.9720	3.0820
10	0.6540	0.6041	55	0.9790	3.3700
15	0.7500	0.9050	60	0.9850	3.7200
20	0.8200	1.2240	65	0.9890	4.0121
25	0.8700	1.5440	70	1.0000	-
30	0.9040	1.8450	75	-	-
35	0.9310	2.1760	80	-	-
40	0.9480	2.4600	--	-	-
		For particle size 3.05×10^{-3} cm			
2	0.3400	0.1226	45	0.9720	3.0813
5	0.5210	0.3330	50	0.9805	3.4204
10	0.6800	0.6750	55	0.9860	3.7701
15	0.7802	1.0283	60	0.9900	4.1100
20	0.8450	1.3698	65	1.0000	-
25	0.8902	1.7111	70	-	-
30	0.9230	2.0660	75	-	-
35	0.8450	2.4027	80	-	-
40	0.9610	2.7465	--	-	-

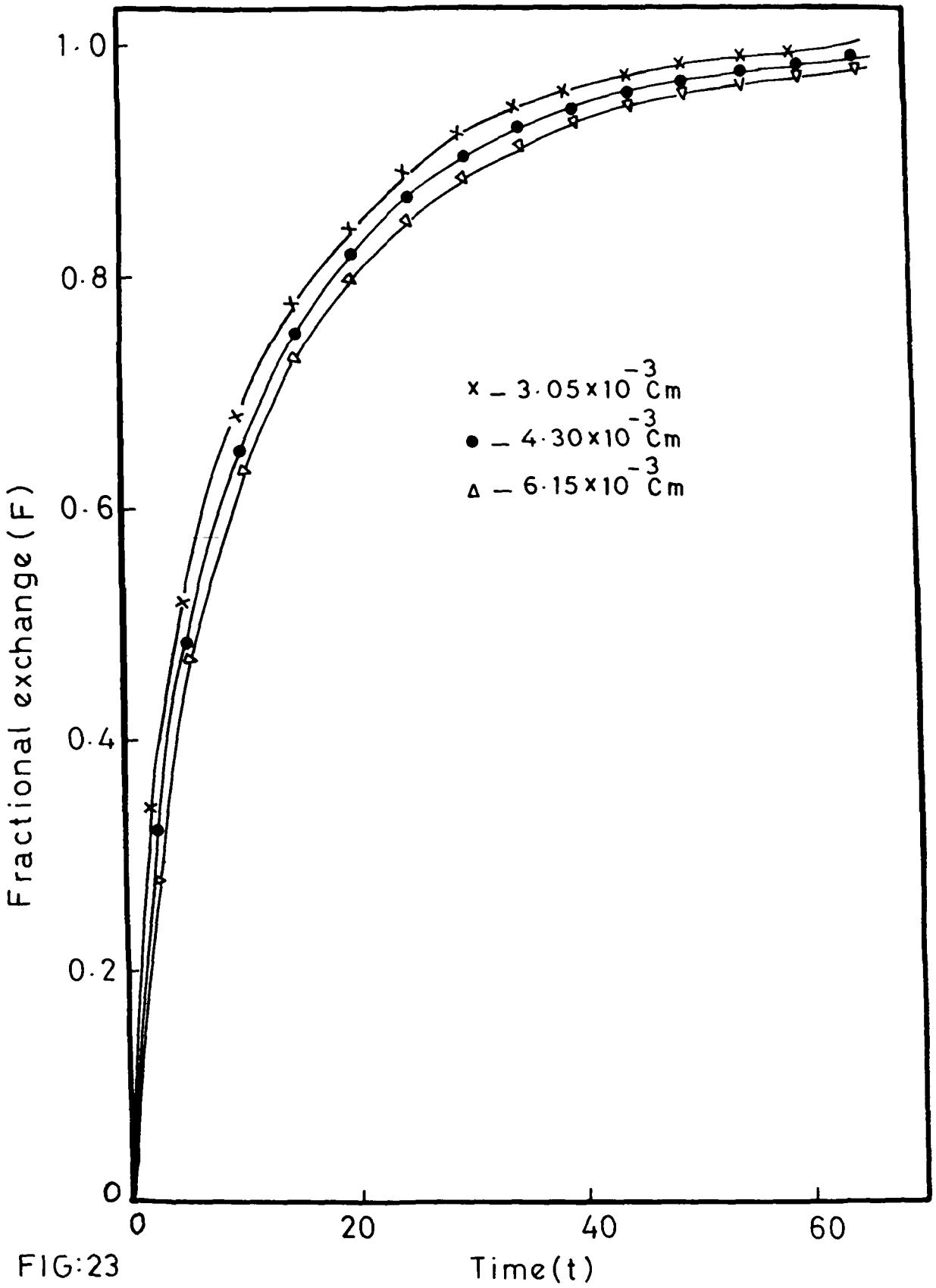

FIG:23

Influence of particle size on the rate of CrO_4^{2-}–NO_3^- exchange at 40°C on thorium-tetracyclohexylamine.

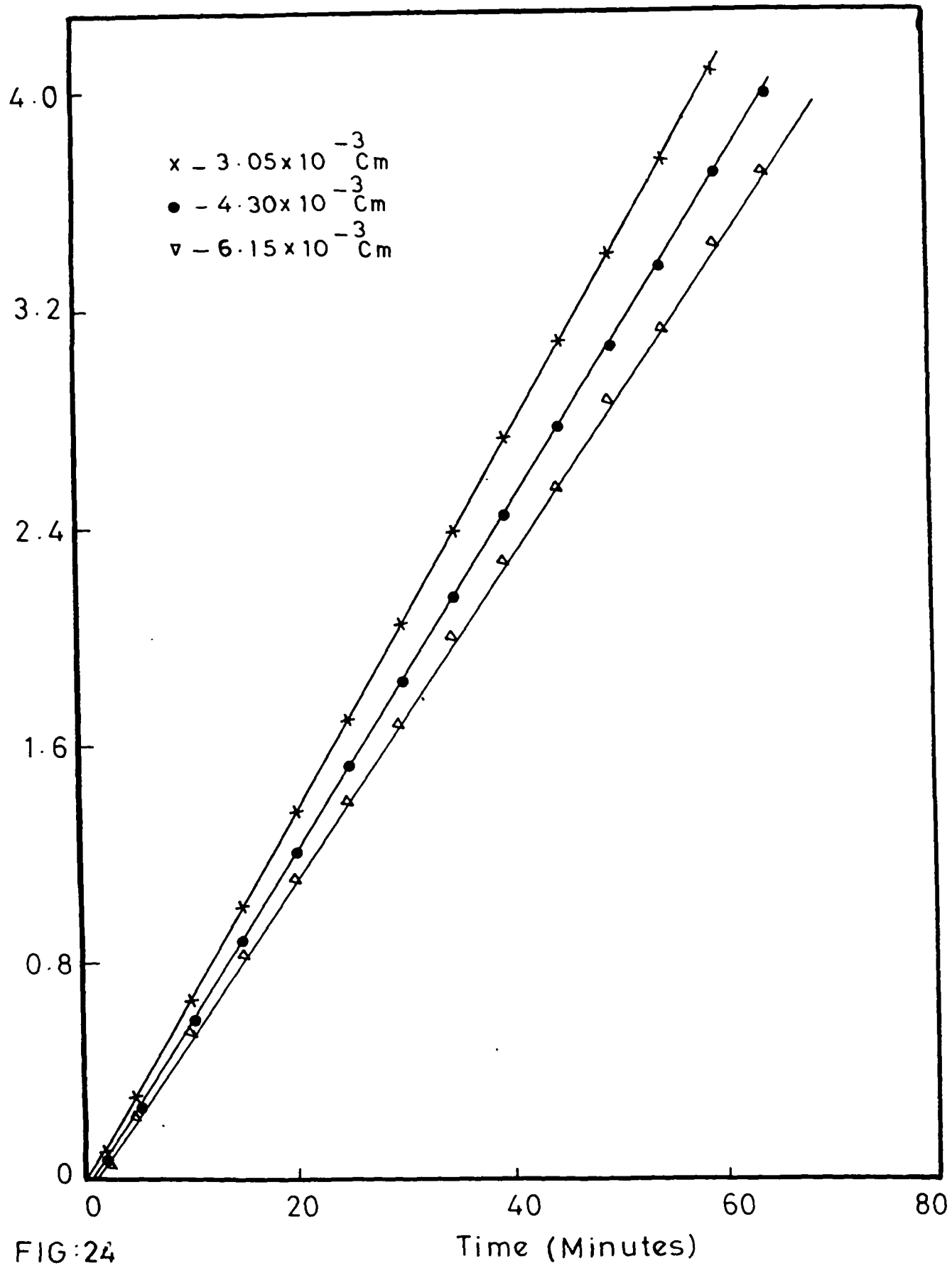

FIG:24

Influence of particle size on the rate of CrO_4^{2-}–NO_3^- exchange at 40°C on thoriumtetracyclohexylamine

DISCUSSION

There are mainly two types of diffusion processes 'film diffusion' and particle diffusion. In film diffusion process, the exchange rate is proportional at least initially to the concentration of ingoing ion, while the particle diffusion controlled phenomena is favoured by high metal ion concentration, relatively large particle size and the vigrous shaking of the exchanging mixture, under these conditions, the fractional attainment of equilibrium with time is given by

$$F = \frac{\text{the amount of exchange at time (t)}}{\text{the amount of exchange at infinite time (equilibrium)}}$$

The interruption test is the best experimental approach for distinguishing between film and particle diffusion control phenomena. Therefore this test was applied for CrO_4^{2-} ions. Results summarized in table 17 and 17a and plotted in figure 15 show an enhanced rate after 10 minutes of interruption which indicates a momentary exchange after reimmersion and hence the rate should be controlled by particle diffusion. This is because the concentration gradient disappears in the particle during the interruption and on reimmersion are much greater than before. Thus, on this basis, it was concluded that the mechanism of exchange is controlled by particle diffusion and hence the experimental conditions were set to explain this phenomena. The equations developed by Boyd et al[15] and improved by Reichenberg were used to calculate the kinetic parameters.

The F values at different time intervals and different temperatures obtained for CrO_4^{2-}, MnO_4^-, Cl^- and $SCN^- - NO_3^-$, exchange are plotted in figures 16-18. These results show that the rate of exchange is directly proportional to the temperature. As the temperature increases, the mobility of ions increases as well as rate of exchange also increases. These curves also show that initially the uptake of ion is rapid. The uptake of ions decreases with increase in time. These results are analogous with that of Heitner and Markovits[16].

As the rate determining step is through ion exchanger particle, the following equation is valid

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\alpha} \frac{\exp(-n^2 Bt)}{n^2} \qquad (1)$$

where

$$B = \frac{\pi^2 di}{r^2} \qquad (2)$$

where r, is the radius of the particle, Di is the effective diffusion coefficient of two exchanging ions inside the resin phase[17] and t, is the time. The typical Bt Vs t plots at three different temperatures viz 40, 50 and $60\pm1^{o}C$ for CrO_4^{2-}, MnO_4^-, Cl^- and SCN^-- NO_3^- exchange given in figures 19-22 show that the rate of exchange is directly proportional to temperature. In all cases the plots of Bt Vs t are linear passing through the origin. This further indicates that the rate determining step is through the particle at all temperatures studied.

Particle size also has a marked effect on the rate of exchange. The F values for CrO_4^{2-} - NO_3^- exchange on exchanger particle of different sizes are plotted in figure 23. While the results of Bt Vs t are given in table 21 and plotted in figure 24. These results show that the rate of exchange is inversely proportional to the particle radius. Equation (2) is used for the calculation of diffusion coefficient (Di). The results of (Di) are given in table 22.

Table 22

Values of Di (cm^2 sec^{-1}) of various anions at different temperatures on thoriumtetracyclohexylamine

Anion	40°C	50°C	60°C
CrO_4^{2-}	6.691×10^{-7}	7.72×10^{-7}	8.235×10^{-7}
MnO_4^-	5.662×10^{-7}	6.176×10^{-7}	7.206×10^{-7}
Cl^-	4.632×10^{-7}	5.147×10^{-7}	5.662×10^{-7}
SCN^-	4.118×10^{-7}	4.632×10^{-7}	5.147×10^{-7}

The linear relationship between - log Di Vs I/T °K (figure 25) enables the calculation of energy of activation (Ea) from the Arrhenius equation.

$$Di = Do \exp(-Ea/RT) \qquad (3)$$

The energy of the anion diffusion process reflects the ease

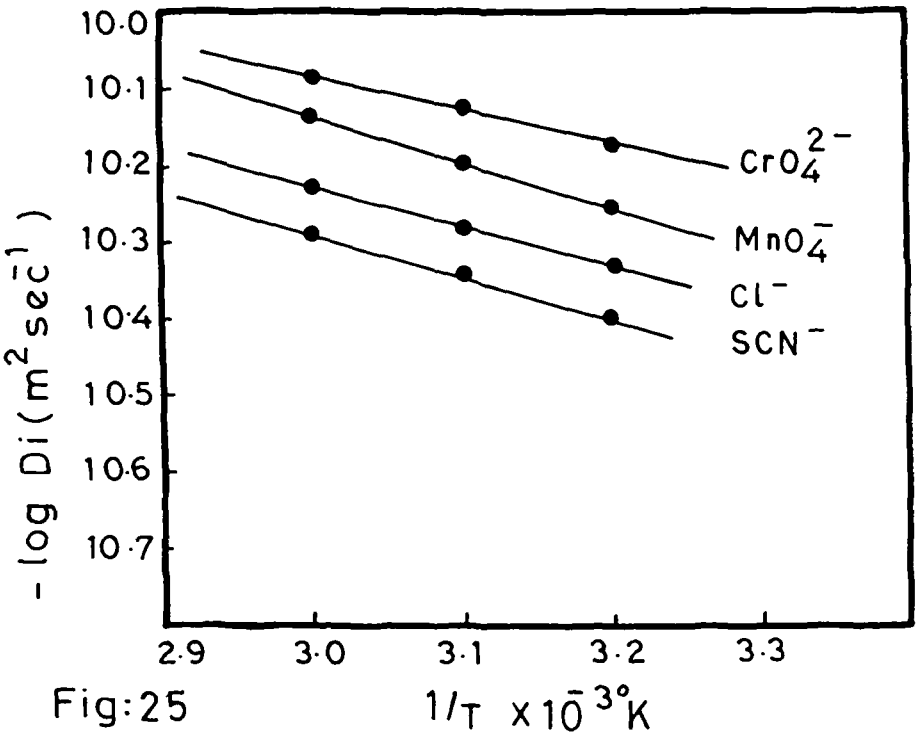

Fig:25

Plots of log Di Vs $1/T$ °K on thorium-tetracyclohexylamine

with which anion can pass through the exchanger. The values of energies of activation are given in table 23. On extrapolating the plot of - log Di Vs 1/T ^{o}K (figure 25) log Do values can be calculated. Substitution of these values in equation (4) gives the entropy of activation (ΔS^{*})

$$Do = 2.72\ d^{2}\ KT/h\ \exp\ (\Delta S^{*}/R) \qquad (4)$$

where d is the ionic jump distance assumed equal to $5x10^{-10}$ cm, K is the Boltzman constant equal to $1.38x10^{-23}$ J. K^{-1} $mole^{-1}$. h, is the plancks constant equal to $6.6x10^{-34}$ J. sec. T, is the absolute temperature equal to 273 ^{o}K and R is the gas constant equal to 8.31 J K^{-1} $mole^{-1}$. The values of Do and ΔS^{*} are given in table 23. These values give a very similar pattern to that obtained with other inorganic ion exchangers[7-8].

Table 23

Self diffusion coefficient, energy of activation and entropy of activation of various anions on thorium-tetracyclohexylamine.

Anions	Do (m^{2} sec^{-1})	Ea K.J $mole^{-1}$	ΔS^{*} J. deg^{-1} $mole^{-1}$
CrO_4^{2-}	$3.631x10^{-9}$	17.35	-58.007
MnO_4^{-}	$3.467x10^{-9}$	21.58	-58.390
Cl^{-}	$3.390x10^{-9}$	16.81	-58.580
SCN^{-}	$3.236x10^{-9}$	18.76	-58.960

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C H A P T E R - IV

SYNTHESIS AND CHARACTERIZATION OF MOLYBDENUM-BENZOINOXIMATE AND ITS USE AS ELECTRON ION EXCHANGER

The analytical applications of ion exchangers are increasing at an exponential rate, and newer areas of their use are being actively sought. Many synthetic inorganic ion exchangers have been used as electron ion exchangers[1-6] and as redox ion exchangers[7-10]. The chemical reductions are important processes in modern industries. Electron ion exchangers are important due to their insolubility in the redox medium. This facilitates their removal from the reaction medium without causing any chemical perturbation to the redox medium.

In the present work, a new electron ion exchanger is synthesized by the reaction of α-benzoinoxime and molybdate. Many oximes possess valuable analytical properties. They form salts either by the replacement of a hydrogen from the oxime or by coordination to the oxime nitrogen. Several transition metal complexes of different oximes have been reported[11-13] and characterized. A survey of literature shows that not much work has been done on α-benzoinoxime derived from α-acyloinoximes Besides other important reactions and properties of these oximes, their reducing properties are worth mentioning. It was in this light that oxime was complexed with molybdenum, whereby it, with its reducing properties reduced molybdenum from an oxidation state of six to an oxidation state of five. Molybdenum by itself, is also a reducing agent, when the complex is brought in contact with an aqueous solution of a reducible species

(copper as an example) the Mo(V) is reconverted to Mo(VI) by a redox reaction whereby copper (II) is reduced to the cuprous ion and molybdenum is oxidized and attains its maximum oxidation state (six). It was therefore considered worthwhile to carry out electron exchange studies on this material. In the present work, the material prepared by α-benxoinoxime and molybdate has been utilized as electron ion exchanger and the reductions of Cu^{2+}, Cr^{6+}, Ce^{4+}, V^{5+}, Fe^{3+}, As^{5+} and Sn^{4+} have been successfully achieved on the columns of this material.

EXPERIMENTAL

Reagents: Sodium molybdate, VEB Labor chemic Apolda (Germany), α-benzoinoxime, Riedel (Germany) were used. All other chemicals used were of A.R. grade.

Synthesis:

Molybdenum-benzoinoximate was synthesized by mxing 0.10 M solution of sodium molybdate to 0.10 M alcholic solution of α-benzoinoxime in the volume ratio of 1:2. The PH of sodium molybdate and ligand solution was set at 1.5 by adding HCl. The initial white precipitate obtained on mixing the two slowly and completely changed to yellowish green after 2 h of continuous stirring. It was then filtered and washed with 3:1 water-alcohol mixture and dried in air oven at 40°C. The results of the synthesis of molybdenum-benzoinoximate are given in table 24.

RESULTS

Table 24

Conditions for the synthesis of Molybdenum-benzoinoximate

S.No.	Conditions of Synthesis Molarity of Reagents		Mixing ratio	pH	Properties
	Sodium-molybdate (M)	α-benzoinoxime (M)			
1.	0.10	0.10	1:1	1.5	Dissolution of precipitate on standing.
2.	0.10	0.10	1:2	1.5	Yellowish green colored precipitate
3.	0.10	0.10	1:2	4.0	Incomplete precipitation
4.	0.10	0.10	1:3	1.5	Blue colored precipitate
5.	0.10	0.10	2:1	1.5	Dissolution of precipitate on standing
6.	0.10	0.10	3:1	1.5	Dissolution of precipitate on standing

Chemical stability:

In order to check the chemical stability 0.500 g of this material was shaken for 6 h. in the desired solution and then the supernatant liquid was checked for molybdenum and α-benzoinoxime.

Conductometric titrations:

Freshly prepared α-benzoinoxime solution was always used for conductometric titrations. The stock solution of sodium molybdate was prepared in 3:1 water-alcohol mixture.

Rate of reduction:

In order to determine the rate of reduction, weighed amount of the exchanger was shaken with the concerned solution, after appropriate intervals of time, the contents of the flask were filtered and the reduced species were determined. The results are plotted in figure 26.

Redox Studies:

Reductions of Cu^{2+}, Cr^{6+}, Ce^{4+}, V^{5+}, Fe^{3+}, As^{5+} and Sn^{4+} in their respective lower oxidation states were performed by passing their solutions through the column containing 0.500 gm of the exchanger. The reductions were performed in CO_2 atmosphere and the effluent was collected in H_2SO_4. The results are given in tables 25-31.

Table 25

Reduction of Cu(II) to Cu(I)

S.No.	Amount of exchanger taken (g)	Amount of Cu(II) taken (mg)	Amount of Cu(I) found (mg)	Standard deviation
1.	0.500	98.00	98.00	
2.	0.500	110.00	109.50	
3.	0.500	140.00	138.70	
4.	0.500	280.00	277.00	1.270
5.	0.500	330.00	326.00	
6.	0.500	370.00	368.10	

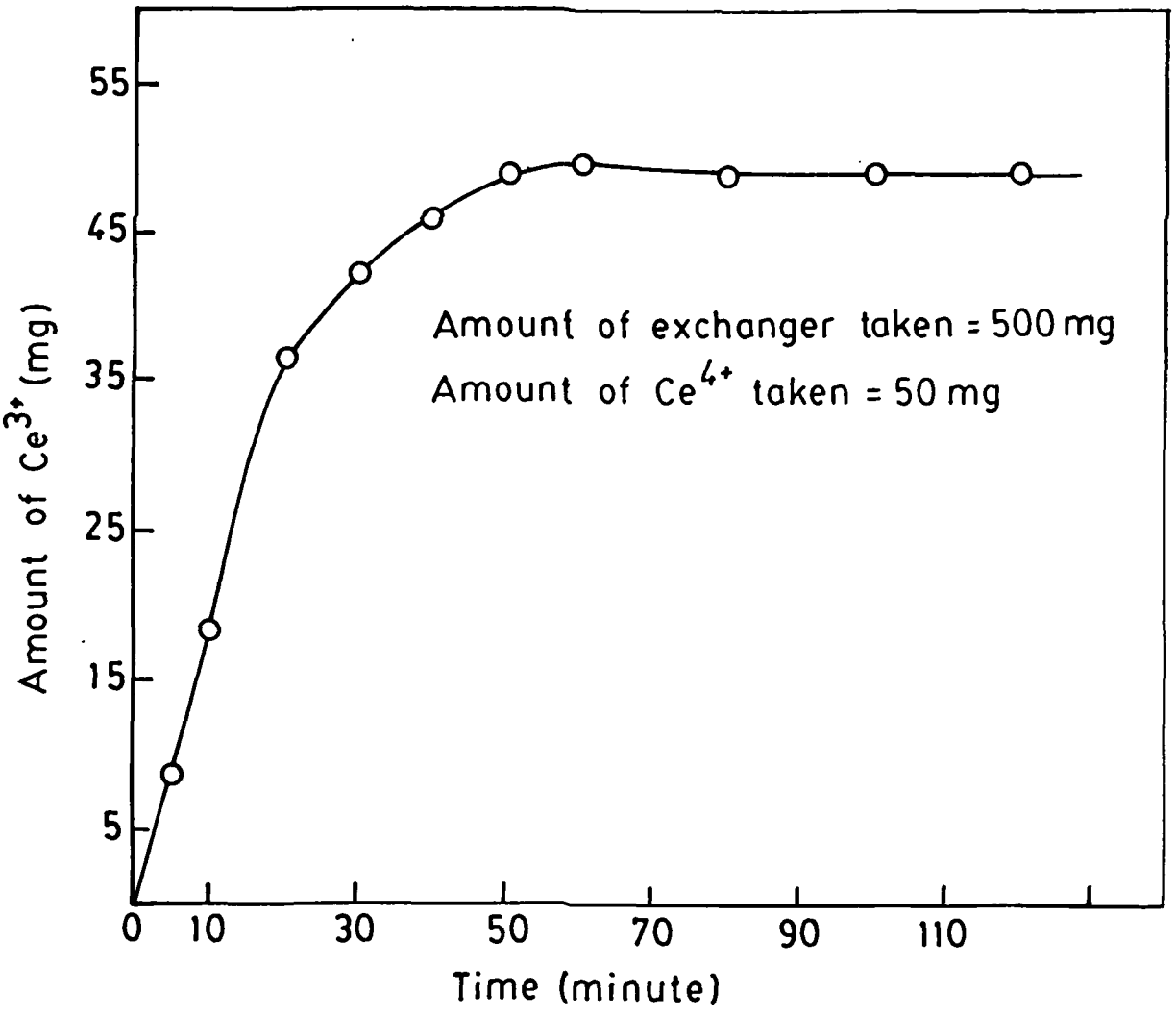


Fig:26 – Plot of rate of reduction of Ce^{4+} to Ce^{3+} by batch process

Table 26

Reduction of Cr(VI) to Cr(III)

S.No.	Amount of exchanger taken (g)	Amount of Cr(VI) taken (mg)	Amount of Cr(III) found (mg)	Standard deviation
1.	0.500	102.00	99.50	
2.	0.500	142.00	139.00	
3.	0.500	166.00	164.00	
4.	0.500	208.00	204.60	0.804
5.	0.500	230.00	228.10	
6.	0.500	246.00	245.00	

Table 27

Reduction of Ce(IV) to Ce(III)

S.No.	Amount of exchanger taken (g)	Amount of Ce(IV) taken (mg)	Amount of Ce(III) found (mg)	Standard deviation
1.	0.500	43.00	41.80	
2.	0.500	68.00	67.80	
3.	0.500	73.00	72.00	
4.	0.500	89.00	87.00	1.160
5.	0.500	134.00	131.00	
6.	0.500	164.00	162.40	

Table 28

Reduction of V(V) to V(IV)

S.No.	Amount of exchanger taken (g)	Amount of V(V) taken (mg)	Amount of V(IV) found (mg)	Standard deviation
1.	0.500	81.00	80.70	
2.	0.500	102.00	102.00	
3.	0.500	143.00	139.60	1.570
4.	0.500	182.00	179.00	
5.	0.500	225.00	224.00	
6.	0.500	250.00	246.00	

Table 29

Reduction of Fe(III) to Fe(II)

S.No.	Amount of exchanger taken (g)	Amount of Fe(III) taken (mg)	Amount of Fe(II) found (mg)	Standard deviation
1.	0.500	34.00	34.00	
2.	0.500	68.00	66.90	
3.	0.500	100.00	99.00	1.050
4.	0.500	134.00	132.00	
5.	0.500	201.00	198.00	
6.	0.500	230.00	227.00	

Table 30

Reduction of As_5(V) to As(III)

S.No.	Amount of exchanger taken (g)	Amount of As(V) taken (mg)	Amount of As(III) found (mg)	Standard deviation
1.	0.500	10.00	9.50	
2.	0.500	30.00	27.00	
3.	0.500	40.00	38.00	1.090
4.	0.500	80.00	78.20	
5.	0.500	100.00	97.30	
6.	0.500	120.00	118.00	

Table 31

Reduction of Sn(IV) to Sn(II)

S.No.	Amount of exchanger taken (g)	Amount of Sn(IV) taken (mg)	Amount of Sn(II) found (mg)	Standard deviation
1.	0.500	80.00	79.00	
2.	0.500	120.00	119.00	
3.	0.500	179.00	179.00	1.240
4.	0.500	198.00	196.30	
5.	0.500	230.00	227.00	
6.	0.500	245.00	241.40	

Electronic and IR spectra:

The electronic spectra was monitored in the range 200-800 nm by Bausch and Lomb Spec. 1001. The solvent used was DMSO (Baker Analyzed Reagent). The IR spectra was recorded by the standard KBr disc method. The IR spectra of the complex is plotted in figure 27.

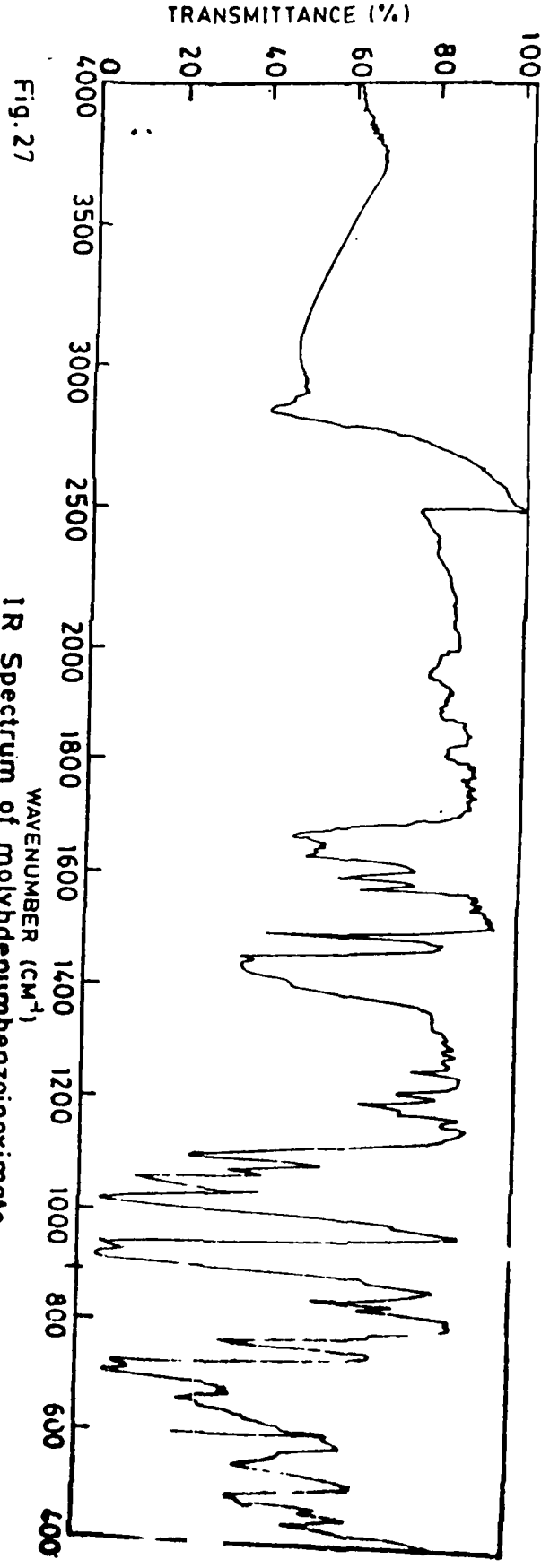


Fig.27

IR Spectrum of molybdenumbenzoinoximate

DISCUSSION

The conditions under which molybdenum-benzoinoximate was synthesized are given in table 24. For complete precipitation of molybdenum-benzoinoximate, equimolar solutions of sodium molybdate (PH=1.5) and α-benzoinoxime (PH=1.5) were mixed in 1:2 volume ratio. It was found that any alteration in PH of these solutions resulted either in dissolution or incomplete precipitation, while alteration in the volume ratio resulted in the formation of blue colored precipitate which was found ineffective for reduction purposes. The yellowish-green precipitate gave good reduction properties. The gradual change from an initial white to yellowish green color is probably due to the slow reduction by α-benzoinoxime of Mo(VI) to Mo(V).

The material, molybdenum-benzoinoximate was found to be quite stable in de-ionized water, ethyl alcohol, methyl alcohol, acetone and dilute solution of acids and bases but is sparingly soluble in chloroform and carbon tetrachloride, and soluble in Dimethyl Sulphoxide (DMSO).

The conductometric titrations show sharp peaks leading to the metal ligand ratio of 1:2. The results of ratio were further confirmed by elemental analysis.

Spectroscopic studies:

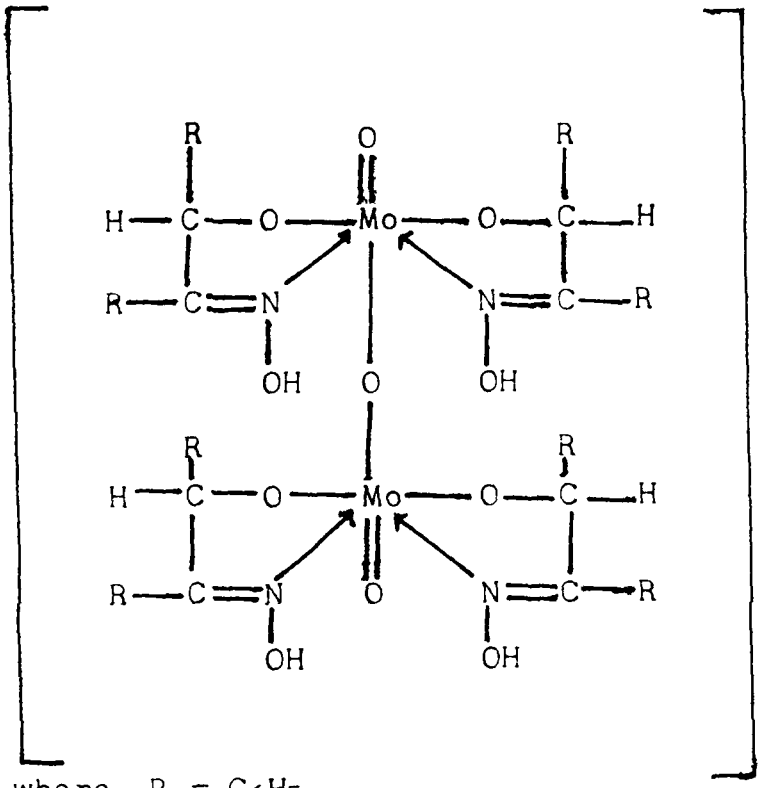
It is quite evident from the infrared spectra (figure 27) that the exchanger exhibits all fundamental bands characteristics of C = N, C = O, Mo = O and Mo = N vibrations. The structure of molybdenum-benzoinoximate is highly complicated like other oxime complexes with other metal ions. An indication of the

possible structure may be discussed in the light of its IR spectrum. It is quite evident from the spectrum of the complex that the phenolic hydrogen of oximate is replaced by the metal because the band at 3200 cm^{-1} does not appear in the complex while it can very well be seen in the spectrum of the ligand. A peak at 1610 cm^{-1} assigned to C = N stretching is shifted to 1640 cm^{-1} and the peak at 985 cm^{-1} of medium intensity in the ligand assigned to N - O stretching vibration shifts to 1005 cm^{-1} in the complex. These changes in the absorption frequencies of C = N and N - O give a good indication for the donation of lone pairs from the nitrogen to the metal to form chelate. The IR spectrum also shows well resolved doublet at 920 and 960 cm^{-1} indicating an Mo - O - Mo bridging[14-16]. The Mo- N bending is indicated by a weak band at 500 cm^{-1}.

The electronic spectrum recorded in DMSO shows two bands at 630 and 670 nm of very low intensity, which may be due to ligand field transition characteristic of Mo(V) in an octahedral array of ligands. However, the μ eff. value is only 0.4 BM (Bohr Magneton) which is very low from that expected for d^1 system[17]. Lowering in magnetic moment values from theoretically expected values may also be due to the existance of Mo - O - Mo bridging similar to that reported in MoO_3Cl_4 (bi py)$_2$ complex[18].

Thus on the basis of the above discussion and elemental

analysis, the following structure for the complex seems plausible.



where R = C_6H_5

Redox Studies:

It is clear from figure 26 that only 50 minutes are required for the complete conversion of Ce^{4+} to Ce^{3+}. The results of table 25-31 show that the material molybdenum-benzoinoximate has a remarkable reducing property. We have utilized this material for the reduction of Cu^{2+}, Cr^{6+}, Ce^{4+}, V^{5+}, Fe^{3+}, As^{5+} and Sn^{4+} to their respective lower oxidation states. It was found that this material could not be used for the reduction of Ti(IV) to Ti(III) which has a redox potential equal to 0.06 but it can reduce Sn^{4+} to Sn^{2+}

which has redox potential equal to 0.10, on this basis it was concluded that molybdenum/benzoinoxime couple has a redox potential somewhere between 0.06 - 0.10 and it can reduce only those substances which have redox potential higher than its own. After reducing a substance, molybdenum-benzoinoximate gets oxidized, it can be re-reduced by passing 0.10 M solution of thiosulfate. For regeneration of 0.500 g of this exchanger about 50 ml of 0.10 M solution of thiosulfate should be passed through the column at the rate of 0.50 ml per minute.

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C H A P T E R - V

RECOVERY OF SILVER FROM LABORATORY WASTES

In laboratories and industries many reagents and chemicals are thrown unknowingly in daily routine as waste. Some of these substances may be of enormous importance if they can be converted in usable forms. Unwisely thrown silver in the form of silver chloride is one such example[1-5]. The material is descarded after quantitative and qualitative analysis. The commercial realization of ion exchange technology to this end may be helpful in many ways. As AgCl is sparingly soluble salt, it might be possible thoeretically to recover silver from it, using a cation exchanger by taking silver ions and thus enabling silver chloride to dissociate further as required by the following equilibrium which

$$AgCl\ (Solid) \rightleftharpoons Ag^{+} + Cl^{-}$$

should shift towards right hand side when Ag^{+} is taken up by the cation exchanger. However, practically this is less feasible.

Perman has tried to recover silver by converting silver chloride into silver amine complex and then reducing with ascorbic acid[6]. Similarly, so many other methods have been developed to recover silver from its impurities, commercial electrolytic silver may contain 0.5% of impurities and silver prepared in dry way is of still lower degree of purity. The impurities which have been reported include lead, copper, gold, bismuth, antimony, arsenic platinum, sulfur etc. A common method of purifying silver is to dissolve it in dilute nitric acid

and precipitate the silver as silver chloride and subsequently reduce the silver chloride to metal Ag to readily reduced from most of its compounds.

V. Kihlschutter and E. Eydmann[7] reduced silver oxide, nitride, hyponitrites, Nitrite, Carbonate and Chromate by the mere application of heat and also by warming the oxide in hydrogen or carbon monoxide. P. Laur[8] found that hydrogen developed in the liquid in which the silver sulphide, chloride, Bromide, and Iodide is suspended reduces these salts to metal. According to Jaques[9], a solution of silver acetate is reduced by hydrogen which H. Vogel[10] found that the same solution is reduced when boiled. F. Mohr[11], reduced the Chloride by mixing it with one third of its weight of resin and gradually raising its temperature when resin is burned away some borax is added and the mixture is heated to the melting point of the metal. The process is very messy. G.C. Wittstein[12] used wood charcoal in place of resin. The reduction is ascribed wholly to the hydrogen of charcoal, for (a) no chloride is evolved, but HCl alone is given off and (b) no reduction occurs, if pure Carbon be substituted for charcoal. J.S. Stas[13] recommended the remelting of metal with 5% borax and 1/2% of soda Nitre in an unglazed procelain Crucible.

J. Thallwiz[14] mixed wood charcoal and sodium dioxide with the silver chloride in a clay crucible. In a short time, a vigorous reaction sponataneously occured and a button of Ag was formed.

J.L. Gay Lussac[15] reduced AgCl by heating it with a mixture of Calcium oxide and Charcoal but according to J.B. Trommsdroff and P.T. Mecssu. t[16] the reaction is incomplete.

Moist AgCl is reduced to metal when placed in contact with iron or Zinc, a little dilute H_2SO_4 or HCl hastens the reactions. The reduced silver is washed with dilute acid than with hot water and dried. It then appears as soft grey powder. It is mixed with borax and then a little nitre added and fused. According to F. Mohr and W. Gregory, the reaction is incomplete and washing with acid does not remove all zinc or iron from the silver. A Gawalowsky[17] also studied the reduction of AgCl by Zinc.

M. Gragor[18] reduced solution of AgCl in liquid ammonia with zinc and found that silver is simultaneously separated from copper, if present. The AgCl can also be triturated with an excess of Hg. A silver amulgum is formed from wich the Hg can be separated by distillation just like the amalgamation process.

The methods described above for the recovery of silver from waste are quite tedious and are unsatisfactory because of poor yield and low purity. In order to over come these difficulties, a simple and inexpensive procedure following ion exclusion combined ion exchange has been applied for the recovery of silver from laboratory wastes silver chloride residues. The yield is 87-91% as silver nitrate and also the purity is quite high.

PROCEDURE

The silver chloride residue, obtained from undergraduate laboratories as waste was acidified with hydrochloric acid to ensure complete precipitation of silver as silver chloride. It was heated at 100°C until residue appeared white. After cooling, the supernatant liquid was decanted and silver chloride was filtered off on whatmann No. 42 paper on a Buchner funnel.

The silver chloride was transferred to a beaker and 25% ammonia solution was added until dissolution was complete. In order to make this solution chloride ion free, it was passed over an anion exchange resin column in nitrate form (Fig. 28, Step 1). The effluent obtained was then passed over cation exchanger in H^+ form resulting the breakage of the silver amine complex. The flow rate was adjusted to 0.5 ml/min. The silver and ammonium ions were eluted with 0.50 M nitric acid (Fig. 28, Step 2). The effluent so obtained was again passed over a cation exchange resin column in ammonium form. As a result of ion exclusion the ammonium ions move faster leaving behind Ag^+ which is exchanged on the column. Ammonium ions were collected as an effluent in a separate beaker. Now ensure for complete exchange of NH_4^+ by Ag^+. After passing all the solution of silver and ammonium the column was thoroughly washed with dionized water to remove silver and ammonium ions sticking the glass wall and the exchanger. The silver was then eluted with 0.50 M nitric acid (Fig. 28, Step 3). The

effluent so obtained was evaporated till all the water was removed leaving salt in the beaker, salt was melted at 280-300^{o}C till brown fumes cease. It was then cooled and treated with water and evaporated over a controlled temperature bath.

The bright shining silver nitrate so obtained was taken out with the help of a spatula.

The flow sheet diagram (Fig. 28) summarizes the whole procedure.

RESULTS

The efficiency of this method was checked by taking known amount of silver nitrate. 50 ml of a standard solution of silver nitrate containing 0.700 gm of Silver nitrate was precipitated with sodium chloride solution. The precipitate so obtained was treated in the way as the waste collected following the recommended procedure. The silver nitrate obtained in the end was weighed and also titrated after dissolving a part of it. The results are summarized in table 32.

Flow chart of ion exchange procedure.

Step 1

$$AgCl + NH_4OH \rightleftharpoons Ag(NH_3)_2Cl + H_2O$$
$$Ag(NH_3)_2Cl + RNO_3^- \rightleftharpoons Ag(NH_3)_2NO_3 + RCl^-$$

Step 2

$$Ag(NH_3)_2NO_3 + RH^+ \rightleftharpoons RAg(NH_3)_2^+ + HNO_3$$
$$R\,Ag(NH_3)_2^+ + HNO_3 \rightleftharpoons AgNO_3 + NH_4NO_3 + RH^+$$

Step 3

$$AgNO_3 + NH_4NO_3 + RNH_4^+ \rightleftharpoons RAg^+ + NH_4NO_3$$
$$RAg^+ + HNO_3 \rightleftharpoons AgNO_3 + RH^+$$

FIGURE : 28

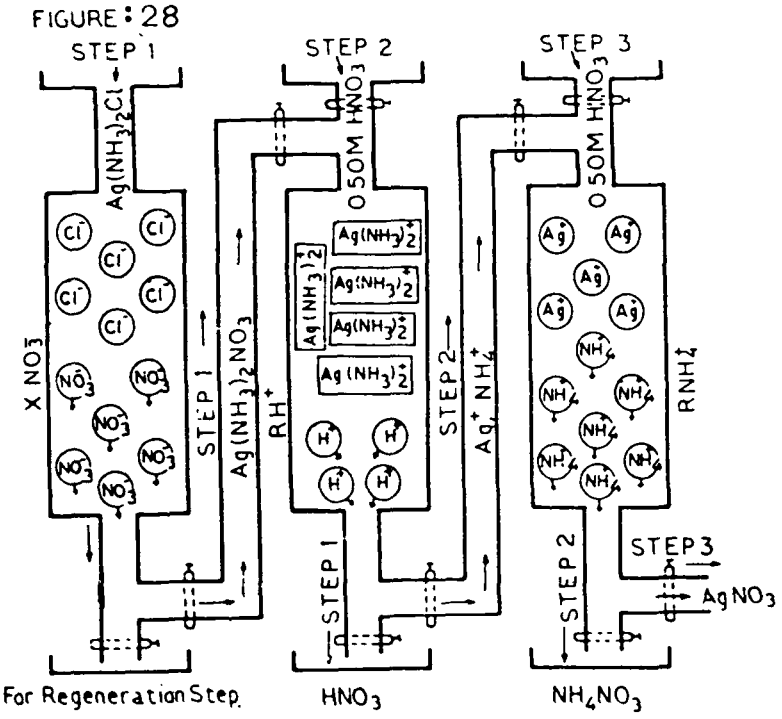

Table 32

No. of observations	Amount of $AgNO_3$ taken	Amount of $AgNO_3$ found	Yield %
1.	0.700 gms	0.602 gm	86%
2.	0.700 gms	0.637 gm	91%
3.	0.700 gm	0.620 gm	89%
4.	0.700 gm	0.603 gm	86.2%
5.	0.700 gm	0.595 gm	85%

These results show that the method is quite successful for recovering Ag^+ as silver nitrate from laboratory wastes.

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Recovery of Silver from Laboratory Wastes

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A simple and inexpensive procedure combining ion exclusion with ion exchange has been applied for the recovery of silver from silver chloride residues in laboratory wastes. The yield is 87–91% as solid silver nitrate.

In laboratories many reagents and chemicals are discarded unknowingly in daily routine as wastes. Some of these substances may be of enormous importance if they can be converted in usable forms. Unwisely discarded silver in the form of silver chloride is one such example (*1–5*). The material is discarded after quantitative and qualitative analyses. The commercial realization of ion exchange technology to this end may be helpful in many ways. As AgCl is a sparingly soluble salt, it might be possible theoretically to recover silver from it using a cation exchanger by removing silver ions and thus enabling silver chloride to dissociate further as required by the equilibrium

$$AgCl\ (solid) \rightleftharpoons Ag^+ + Cl^-$$

which should shift toward the right-hand side when Ag^+ is taken up by the cation exchanger. However, practically this is less feasible. Perman has tried to recover silver by converting silver nitrate into a silver amine complex and then reducing with ascorbic acid (*6*). To have a simplified procedure, we have tried the ion exchange combined with ion exclusion in order to get a good yield of silver as silver nitrate.

Procedure

The silver chloride residue obtained from undergraduate laboratories as waste was acidified with hydrochloric acid to ensure complete precipitation of silver as silver chloride. It was heated at 100 °C until the residue appeared white. After cooling, the supernatant liquid was decanted, and silver chloride was filtered off on Whatmann No. 42 paper on a Buchner funnel.

The silver chloride was transfered to a beaker, and 25% ammonia solution was added until dissolution was complete. In order to make this solution chloride-ion-free, it was passed over an anion exchange resin column in nitrate form (step 1 in figure). The effluent obtained was then passed over cation exchanger in H^+ form, resulting in the breakage of the silver amine complex. The flow rate was adjusted to 0.5 ml/min. The silver and ammonium ions were eluted with 0.50 *M* nitric acid (step 2 in figure). The effluent so obtained was again passed over a cation exchange resin column in ammonium form. As a result of ion exclusion, the ammonium ions move faster, leaving behind Ag^+, which is exchanged on the column. Ammonium ions were collected as an effluent in a separate beaker. After passing all the solution of silver and ammonium, the column was thoroughly washed with deionized water to remove silver and ammonium ions sticking to the glass wall and the exchanger. The silver was then eluted with 0.50 *M* nitric acid (step 3 in figure). The effluent so obtained was evaporated until all the water was removed, leaving salt in the beaker; the salt was melted at 280–300 °C until brown fumes ceased (*7*). It was then cooled and treated with water and evaporated over a controlled-temperature bath.

The flow diagram (figure) summarizes the procedure

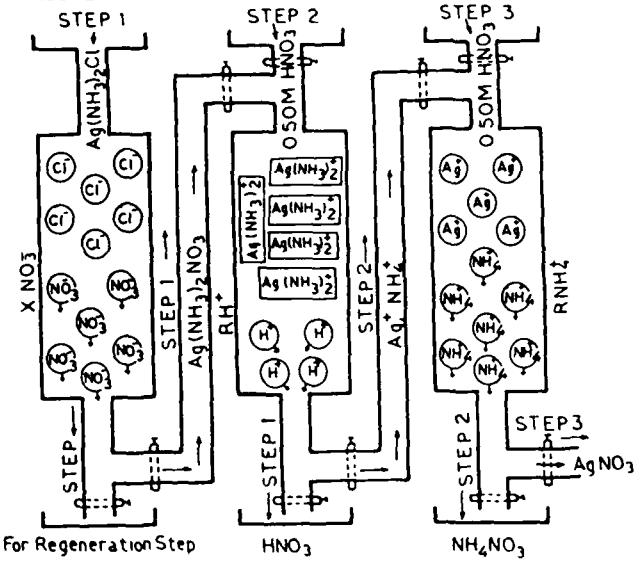
Results

The efficiency of this method was checked by recovering known amounts of silver nitrate. Fifty milliliters of a standard solution of silver nitrate containing 0.70 g of silver nitrate was precipitated with a sodium chloride solution. The precipitate so obtained was treated in the same way as the waste collected following the recommended procedure. The silver nitrate obtained was weighed and also titrated after dissolving a part of it. The results are summarized in the table. These results show that the method is quite successful for recovering Ag as silver nitrate from laboratory wastes.

Results of $AgNO_3$ Recovery

Sample No.	$AgNo_3$ expected (g)	$AgNo_3$ found (g)	Yield (%)
1)	0.70	0.602	86
2)	0.70	0.637	91
3)	0.70	0.62	89
4)	0.70	0.603	86.2
5)	0.70	0.595	85

FIGURE 1



Flow chart of ion exchange procedure

Step 1

$$AgCl + NH_4OH \rightleftharpoons Ag(NH_3)_2Cl + H_2O$$
$$Ag(NH_3)_2Cl + RNO_3^- \rightleftharpoons Ag(NH_3)_2NO_3 + RCl^-$$

Step 2

$$Ag(NH_3)_2NO_3 + RH^+ \rightleftharpoons RAg(NH_3)_2^+ + HNO_3$$
$$Ag(NH_3)_2^+ + HNO_3 \rightleftharpoons AgNO_3 + NH_4NO_3 + RH^+$$

Step 3

$$AgNO_3 + NH_4NO_3 + RNH_4^+ \quad RAg^+ + NH_4NO_3$$
$$RAg^+ + HNO_3 \rightleftharpoons AgNO_3 + RH^+$$

Acknowledgment

The authors are thankful to M. S. Ahmad, Chairman of the Department of Chemistry at A.M.U., for providing research facilities. We extend our thanks to Balbir Singh and Masood Alam for their help during this work. Thanks are also due to the University Grants Commission for financial assistance.

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Is Volume Conserved?

A First General Chemistry Experiment

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In freshman general chemistry courses, the designer of initial laboratory experiments is faced with a dilemma: how to introduce the student to meaningful scientific inquiry while his/her exposure to the fundamental laws of chemistry is just beginning. Many laboratory syllabi deal with this problem by beginning with a largely statistical exercise: weighing pennies, popping popcorn, or the like. While such experiments require little chemistry and have the virtue of stressing variability in scientific measurement, they do not immediately involve the student in the intriguing questions of chemical science.

Ideally, one would like to have a first experiment in general chemistry that introduced the student to scientific methodology, afforded practice in the essential laboratory skills of measurement, and illustrated some fundamental chemical relationship, all without requiring any chemical sophistication or expensive materials and equipment.

An experiment which meets all of these criteria is an exploration of the change of volume upon mixing two common liquids. Such an experiment, as described below, has been used successfully for two years in the Honors General Chemistry Laboratory at California State University, Fullerton. Students are surprised to discover that volume is not conserved under conditions—mixing of similar liquids—where they intuitively expect it to be, and while the details of the interactions causing volume change on mixing are rather sophisticated, the fundamental notions of molecular size and intermolecular forces as determinants of volume are understood by them.

Design of the Experiment

The experiment is designed to be entirely self-contained, except for a single standard: the density of water, which is provided as a graph of density as a function of temperature. Students carry out the following sequence of operations:

1) Calibrate a 10-ml volumetric flask. The flask is weighed dry and filled to the mark with distilled water of measured temperature. The calibration is done at least thrice to establish precision.
2) Determine density of a second liquid. The calibrated flask is filled to the mark with a liquid other than water (acetone, methanol, ethanol, isopropanol, acetonitrile, *p*-dioxane, dimethyl sulfoxide are all suitable) and weighed to obtain the liquid's density.
3) Calibrate a transfer pipet. A 5-ml transfer pipet is used to deliver five successive aliquots of each of the two liquids into a small Erlenmeyer flask, which is weighed before and after each transfer. From mass differences and liquid density, the volume delivered by the pipet is computed.
4) Test for volume conservation. Following the five transfers in step (3), the pure liquid in the Erlenmeyer is used to fill the calibrated volumetric, which is then weighed. From the resulting density and the total mass transferred to the Erlenmeyer, the volume of liquid in the Erlenmeyer is computed and compared to the volume delivered.
5) Prepare liquid mixtures. Using the calibrated transfer pipet, a series of mixtures of the two liquids of varying composition is prepared. Volume proportions are 15+5, 10+5, 10+10, 5+10, and 5+15 ml.
6) Determine density of the mixtures. After thorough mixing and measurement of the temperature, each mixture is used to fill the calibrated volumetric flask to the mark, and it is then weighed.
7) Test for volume conservation. From the pipet volume, the expected total volume of each mixture is computed. From the volumes and densities of pure liquids, the total mass of each mixture is computed. From these masses and densities of the mixtures, the actual volumes of the mixtures are computed and compared with the expected volumes.

Materials and Equipment

Distilled or deionized water: 100–150 ml/student
Acetone for rinsing glassware, optional but convenient
100 ml of any of the following per student:
- Ethanol
- Methanol
- Isopropanol
- Acetonitrile
- Dimethyl sulfoxide
- *p*-Dioxane
- Acetone

One per student of the following:
- 10-ml volumetric flask
- 5-ml transfer pipet
- stoppered 50-ml Erlenmeyer flask
- 0–100° thermometer
- pipet bulb
- Pasteur pipets and rubber bulb
- graph of density of water versus temperature

0.1-mg-precision analytical balance, one for every four students

Computations

The calculations required in this experiment involve either the density equation, $\rho = m/V$, or the law of conservation of mass (additivity of masses), $m_{total} = \sum_i m_i$. The flask calibration (operation (1)) is achieved using known water density and measured masses:

$$V_{flask} = (m_{filled} - m_{empty})/\rho_{water} \quad (1)$$

The density of the second liquid (operation (2)) and of the mixtures (operation (6)) is computed from this calibrated volume and measured masses:

$$\rho_{liquid} = (m_{filled} - m_{empty})/V_{flask} \quad (2)$$